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Division of Chemical Sciences

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Bulletin of the Academy of Sciences of the U.S.S.R., Division of Chemical Sciences, in English Translation
September - October, 1952

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BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR

DIVISION OF CHEMICAL SCIENCES

1952, No. 5

September- October

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NOTE

The organophosphorus nomenclature adopted in this issue is that recommended by the Drake Committee of the American Chemical Society and published in "Chemical and Engineering News", Volume 30, No. 43 (October 27, 1952), pp. 4515-4522. An exception is formed by terms such as "diethylphosphorous acid", a literal translation of the Russian term, which is often used as a convenient, noncommital name for a tautomeric substance (diethyl hydrogen phosphite and/or diethyl phosphonate).

— Publisher.

Dear Aleksandr Ermingeldovich:

The Division of Chemical Sciences and the Editorial Board of the "Bulletin of the USSR Academy of Sciences, Division of Chemical Sciences" warmly congratulate you on the occasion of your seventy-fifth Birthday.

For more than fifty years you have devoted your creative labor to the service of the Fatherland. Your teaching and organizing activities have borne abundant fruit: a great number of investigators and technologists whom you have taught and are now doing valuable work in all spheres of the national economy.

It is our fervent desire, Aleksandr Ermingeldovich, that you may have health, strength, and vigor, so that you may contribute still further to the blossoming forth of our science and our culture in the interests of our people.

Division of Chemical Sciences of the
USSR Academy of Sciences

Editorial Board of the "Bulletin of the USSR
Academy of Sciences, Division of Chemical
Sciences"

ESTERS OF "GLYCOLPHOSPHOROUS ACIDS"

COMMUNICATION 1. COMPOUNDS HAVING FIVE-, SEVEN, AND EIGHT-MEMBERED RINGS

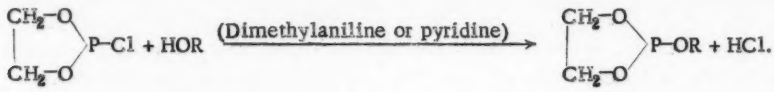
A. E. Arbuzov and V. M. Zoroastrova

The cyclic esters of phosphorous acid have received practically no study until recently. In the literature there are to be found only the reports by Carre [1] of his preparation in 1902 of the acid chloride of "ethylene-glycolphosphorous acid" (ethylene phosphorochloridite) by the action of phosphorus trichloride on ethylene glycol and of the "ethylene-glycolphosphorous acid" itself (ethylene hydrogen phosphite) , the barium salt of which was analyzed. Neither compound was isolated in a chemically pure form.

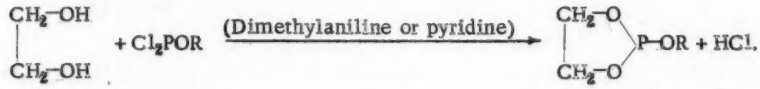
More detailed investigations into cyclic derivatives of phosphorous acid were commenced in our laboratory in 1945 [2]. In the present communication we give the results that we have obtained in a study of compounds containing five-, seven-, and eight-membered rings. By the action of phosphorus trichloride on ethylene glycol, 1,4-butanediol, and diethylene glycol in presence of substances that bind hydrogen chloride, we have synthesized the following phosphorochloridites (Table 1).

Ethylene phosphorochloridite (Compound 1) is a colorless liquid that fumes in air; it is similar in properties to diethyl phosphorochloridite. The phosphorochloridites derived from glycols in which the OH groups are separated by a chain of four or of five atoms (Compounds 2 and 3) contain seven- and eight-membered rings. They are very unstable: they fume strongly in air and, in a thin layer, ignite spontaneously and burn with a blue flame. In the pure state they are colorless liquids, but they rapidly polymerize, even in closed vessels, giving a colorless gelatinlike mass, which later becomes yellow with separation of red phosphorus.

By the action of alcohols in presence of pyridine or of dimethyl-aniline on cyclic phosphorochloridites, mixed cyclic esters are formed:

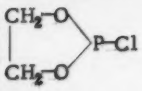
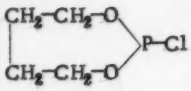
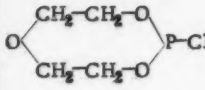


Cyclic esters of phosphorous acid may be obtained also by the action of glycols on Menshutkin's acid chloride in presence of the same acid-binding media:

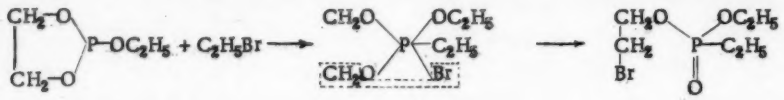


Esters having a seven-membered ring were obtained by the latter method. We did not succeed in obtaining a mixed ester having an eight-membered ring. Six esters, obtained by one or other of the above methods, are listed in Table 2.

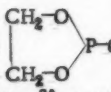
TABLE 1

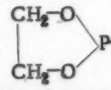
No.	Formula	B.p. °C	Pressure (mm Hg)	d_0^{20}	n_D^{20}	MR_D found	MR_D calculated
1		41.5	10	1.4172	1.4915	25.46	25.53
2		74-75.5	8	1.2858	1.5010	35.33	34.81
3		104-105	15	1.2693	1.5165	40.14	39.43

The physical and chemical properties of the esters obtained depend to a considerable extent on molecular size and structure: the compounds of low molecular weight are in many ways similar to trimethyl phosphite. The mixed cyclic esters of phosphorous acid are extremely reactive compounds. They react vigorously with cuprous halides, giving complex compounds. The CuI complexes of ethylene methyl phosphite and of ethyl ethylene phosphite were obtained in a crystalline form (Compound I, m.p. 132-133°; Compound 2, m.p. about 90°). The cyclic esters react with sulfur with formation of thio esters. They react with water with evolution of much heat, and on coming into contact with concentrated nitric acid they burst into flame. One of the most interesting properties of cyclic phosphorous esters is their ability to react with many substances with opening of the ring. The reaction may be represented as follows:

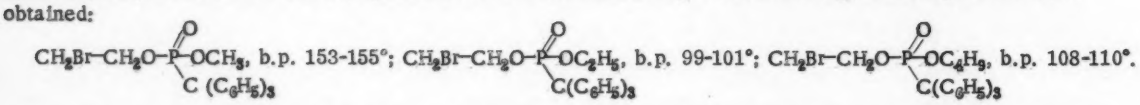


and is a special case of the Arbuzov rearrangement.

By the action of CH_3I on  there was obtained ethyl 2-iodoethyl methylphosphonate: b.p. 138-139°/10 mm; d_0^{20} 1.6783; n_D^{20} 1.4978; found MR_D 48.54; calculated MR_D 48.45. On hydrolysis with 10% hydrochloric acid it yielded methylphosphonic acid. The product of the reaction of CH_3I with ethylene methyl phosphite decomposed when distilled.

The action of C_2H_5Br on  yielded 2-bromoethyl ethyl ethylphosphonate, b.p. 129-139°/11 mm (dec.); d_0^{20} 1.3726; n_D^{20} 1.4610; found MR_D 48.98; calculated MR_D 48.17.

The reactions of the mixed ethylene-methyl, ethyl-ethylene, and butyl-ethylene esters of phosphorous acid with bromotriphenylmethane led also to rupture of the five-membered ring. The following reaction products were obtained:



In the cases that we examined of reactions between the cyclic esters and halogen compounds, the yields were generally low, and they were never quantitative. It cannot therefore be asserted that the reaction proceeds exclusively in one direction, i.e., with rupture of the ring. The mixed ethylene-methyl and ethyl-ethylene esters of phosphorous acid were found to react energetically with acetyl chloride, but we did not succeed in isolating individual compounds owing to decomposition of the reaction products when vacuum-distilled. The analytical figures for chlorine in the fractions separated differed from the calculated values by 2-3%.

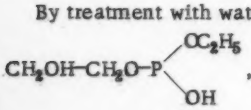
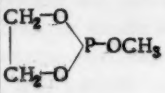
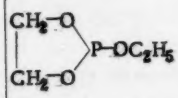
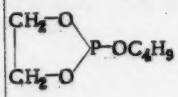
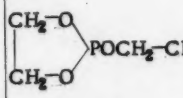
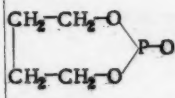
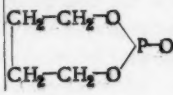
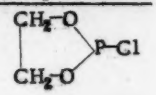
By treatment with water, ethyl ethylene phosphite yielded a product corresponding in analysis to  , b.p. 142-143°/11 mm; n_D^{20} 1.4825. It was a very viscous, colorless liquid.

TABLE 2

No.	Formula	B.p. °C	Pressure (mm Hg)	d_0^{20}	n_D^{20}	MRD found	MRD calculated
1		55-56	23	1.2159	1.4460	26.77	26.91
2		51-51.5	15	1.1317	1.4395	31.66	31.62
3		71-72	8.5	1.0819	1.4470	40.53	40.82
4		78.5-79.5	6.5	1.3206	1.4755	36.39	36.41
5		54-55	4.5-5	1.1640	1.4642	35.60	36.15
6		100-102	9-10	1.0557	1.4540	49.28	50.00

EXPERIMENTAL

1. Preparation of 

Ethylene glycol (77.5 g), dimethylaniline (302.7 g), and dry ether (700 ml) were placed in a two-liter round-bottomed flask fitted with reflux condenser and dropping funnel. The mixture was stirred mechanically and cooled by surrounding the flask with iced water. Freshly distilled phosphorus trichloride (171.7 g) was added dropwise to the mixture. At first, the dimethylaniline hydrochloride formed in the reaction came out in the form of an oil, and this crystallized out only after one-third of the required amount of phosphorus trichloride had been added. Subsequently, the dimethylaniline hydrochloride formed crystallized out immediately. When the whole of the phosphorus trichloride had been added, stirring was continued for a further 45 minutes. The precipitate was then filtered off under suction and was washed well with dry ether. Solvent was distilled off from the filtrate, which was then vacuum-fractionated. The product (113.7 g) had b.p. 38-56°/9 mm; a residue of 21 g remained in the flask. Redistillation through a Widmer column yielded a fraction (101.2 g, 64%) of b.p. 41.5°/10 mm, d_0^{20} 1.4172; n_D^{20} 1.4950; found MR_D 25.46; calculated MR_D 25.58. The substance was a colorless mobile liquid, soluble in organic solvents. It fumed in air and reacted vigorously with water. It was oxidized by concentrated nitric acid with deflagration.

Found %: Cl 27.99

$C_2H_4O_2PCl$. Calculated %: Cl 28.02

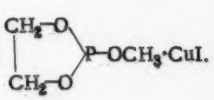
2. Preparation of Ethylene Methyl Phosphite

The materials taken for reaction were ethylene phosphorochloridite (46 g), absolute methanol (11.64 g, i.e. one mole per mole of the chlorido compound), and dimethyl aniline (44.03 g); the methanol and dimethylaniline were dissolved in dry ether (300-280 ml). Ethylene phosphorochloridite, diluted with an equal amount of dry ether, was added dropwise to the snow-cooled solution, which was constantly stirred. As reaction proceeded, the mixture grew warm and a colorless oil separated (dimethylaniline hydrochloride); the latter soon began to crystallize. When the whole of the chlorido compound had been added, the mixture was stirred for a further 20 minutes. The precipitate was filtered off and washed three times with dry ether. The ether solution was fractionated from an Arbuzov flask having two bulbs. After two fractionations a product (21.75 g, 49%) was obtained having b.p. 55-56°/23 mm; d_0^{20} 1.2159; n_D^{20} 1.4460; found MR_D 26.77; calculated MR_D 26.91.

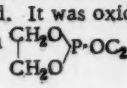
The product was a colorless, very mobile liquid having a very pleasant odor similar to that of trimethyl phosphite; it was soluble in many organic solvents. It reacted with water, producing much heat, and it burst into flame on coming into contact with concentrated nitric acid.

Found %: P 25.33; 25.28

$C_3H_7O_3P$. Calculated %: P 25.41

It reacted with CuI with formation of a crystalline substance, m.p. 132-133° (from chloroform)  .

3. Preparation of Ethyl Ethylene Phosphite

Ethylene phosphorochloridite was added dropwise to a mixture of absolute alcohol (19.27 g), dimethylaniline (50.73 g), and dry ether (300 ml) (mechanical stirring, cooling with snow). Almost from the first drop of the phosphorochloridite a precipitate of dimethylaniline hydrochloride began to form. When the whole of the phosphorochloridite had been added and stirring had been continued for 35 minutes, the reaction was regarded as finished. The dimethylaniline hydrochloride was filtered off, and the filtrate was vacuum-distilled from an Arbuzov flask having two bulbs. The product (31.93 g, 56%) had b.p. 51-51.5°/15 mm; d_0^{20} 1.1317; n_D^{20} 1.4395; found MR_D 31.66; calculated MR_D 31.62. The compound was similar in appearance to ethylene methyl phosphite and had a characteristic odor, not so pleasant as that of the methyl compound. It was oxidized by concentrated nitric acid with deflagration. It formed a complex compound of composition  , m.p. about 90°, unstable in air.

Found %: P 22.89

$C_4H_9O_3P$. Calculated %: P 22.79

4. Preparation of Butyl Ethylene Phosphite

Butyl ethylene phosphite was prepared via Menshutkin's acid chloride. Pyridine was used in place of dimethylaniline, for the boiling point of dimethylaniline is close to that of butyl ethylene phosphite. The materials taken for reaction were: $C_4H_9OPCl_2$ (58.2 g), ethylene glycol (20.62 g), and pyridine (52.57 g). The $C_4H_9OPCl_2$, diluted with an equal volume of dry ether, was added dropwise to a solution in dry ether (300 ml) of the ethylene glycol and pyridine (mechanical stirring, cooling with snow). Pyridine hydrochloride did not begin to crystallize out immediately; crystallization began only after about one-fifth of the necessary amount of acid chloride had been added. The latter was added over one hour, and the mixture was then stirred further at room temperature for 30 minutes. Fractionation of the reaction products (after separation of the precipitate and removal of solvent) yielded a substance (24 g, 44.3% of b.p. 71-72°/8.5 mm, d_0^{20} 1.0819; n_D^{20} 1.4470; found MR_D 40.53; calculated MR_D 40.87. The product was an oily liquid of characteristic odor; it was more viscous than the previous esters.

Found %: P 18.68; 18.86

$C_6H_{13}O_3P$. Calculated %: P 18.90

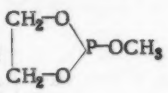
5. Preparation of 2-Chloroethyl Ethylene Phosphite

A mixture of 2-chloroethanol (31.81 g), pyridine (31.24 g), and dry ether (300 ml) was placed in a one-liter flask fitted with reflux condenser, mechanical stirrer, and dropping funnel; the flask was cooled externally with snow. Ethylene phosphorochloridite (50 g), diluted with an equal volume of dry ether, was added over one hour under constant stirring. With the addition of the first drops of phosphorochloridite, a crystalline precipitate of pyridine hydrochloride began to separate from the reaction mixture. The temperature in the flask did not exceed 5°. When the whole of the phosphorochloridite had been added, the reaction mixture was stirred for 15 minutes. The mixture was then allowed to stand without stirring for two hours at room temperature. The pyridine salt was filtered off, and the filtrate was vacuum-fractionated through a Widmer column. A fraction of b.p. 78.5-79.5°/6.5 mm (50 g, 74%) was obtained; d_0^{20} 1.3206; n_D^{20} 1.4755; found MR_D 36.39; calculated MR_D 36.41. It was an oily liquid of characteristic odor, soluble, like the previous esters, in many organic solvents. It reacted vigorously with water.

Found %: Cl 20.62

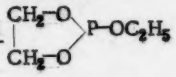
$C_4H_9O_3PCl$. Calculated %: Cl 20.79

Action of Alkyl Halides on the Esters

1. Action of Methyl Iodide on 

A mixture of ethylene methyl phosphite (6.7 g) and methyl iodide (7.8 g, i.e. one mole per mole of ester) was sealed in a tube (the tube was drawn out at one end; the meniscus was in the narrow part of the tube and its position was marked by pencil before the experiment). The tube was allowed to stand at room temperature for 24 hours, when a small diminution in the volume of mixture could be observed. When the tube had been heated at

40° for seven hours and at 60° for one hour, reaction was considered to be complete. When the tube was opened, the odor of the original ester could not be detected. The reaction product was distilled. About 2 g of methyl iodide and 3.7 g of a fraction of b.p. 100-130°/4-5 mm (dec.) (a viscous liquid having an intense iodine color) were obtained. Considerable decomposition was again observed when this fraction was redistilled. We did not succeed in separating any individual substances.

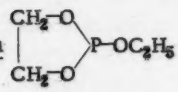
2. Action of Methyl Iodide on 

A mixture of ethyl ethylene phosphite (4.23 g) and methyl iodide (4.41 g) was heated in a sealed tube at 50-60° for 6.5 hrs. The contents of the tube took up the color of iodine. When they were distilled, a red product (2.65 g, 30.6%), b.p. 138-139°/10 mm, was obtained; it was soluble in ether, benzene, and alcohol and had d_0^{20} 1.6783; n_D^{20} 1.4978; found MR_D 48.54; calculated MR_D 48.45.

Found %: I 45.48; 45.55

$C_5H_{12}O_3PI$. Calculated %: I 45.65

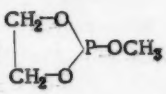
Hydrolysis of product of b.p. 138-139°/10 mm. The product (0.9 g) was heated with 10% hydrochloric acid (10 ml) in a sealed tube at 140° for six hours. Crystals of m.p. 103-105° were obtained (m.p. of methylphosphonic acid: 105°).

3. Action of Ethyl Bromide on 

A mixture of ethyl ethylene phosphite (6.8 g) and ethyl bromide (5.4 g, i.e. one mole per mole of ester) was heated in a sealed tube at 100° for 16 hours. The reaction did not go to completion; the odor of the original ester persisted. Heating of the mixture was continued at 130° for 15 hours. As a result of two fractionations of the reaction products, a fraction (3.8 g, about 35%) was separated having b.p. 129-130°/11 mm (dec); d_0^{20} 1.3726; n_D^{20} 1.4610; found MR_D 48.98; calculated MR_D 48.17. It was a colorless, almost odorless liquid, soluble in the usual organic solvents.

Found %: Br 32.44

$C_6H_{14}O_3PBr$. Calculated %: Br 32.61

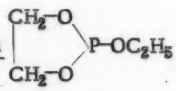
4. Action of $(C_6H_5)_3CBr$ on 

A mixture of $(C_6H_5)_3CBr$ (1 g) and ethylene methyl phosphite (0.37 g, i.e. 1 mol. equiv.) was dissolved in dry benzene (4 ml), and the solution was boiled under reflux for 20 minutes. When reaction was complete, part of the benzene was driven off. The reaction mass crystallized on standing, and the crystals were filtered off and washed with ligroin. After three recrystallizations from a benzene-gasoline mixture, fine colorless prisms, m.p. 153-155°, were obtained. The product was of good solubility in ether, benzene, and chloroform.

Found %: Br 17.15

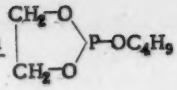
$C_{22}H_{22}O_3PBr$. Calculated %: Br 17.55

Hydrolysis of the reaction product. Some of the product of m.p. 153-155° (0.1 g) was heated in a sealed tube with 10% hydrochloric acid (2 ml) at 180° for five hours. Crystals of triphenylmethylphosphonic acid, m.p. 276-280°, were obtained.

5. Action of $(C_6H_5)_3CBr$ on 

A solution of bromotriphenylmethane (1 g) and ethyl ethylene phosphite (0.38 g) in dry benzene was boiled for 25 minutes. After removal of a part of the benzene, the mixture was poured into a dish and set aside for crystallization, which occurred in the course of a day. The substance was recrystallized from a mixture of benzene and gasoline (0.9 g, m.p. 99-101°). It was similar in its properties to the previous product.

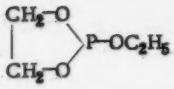
Hydrolysis of the reaction product. Some of the product (0.2 g) was heated with hydrochloric acid (7 ml) at 170-180° for five hours. Triphenylmethylphosphonic acid, m.p. 275-279°, was obtained.

6. Action of $(C_6H_5)_3CBr$ on 

A solution of butyl ethylene phosphite (1.8 g) and bromotriphenylmethane (3.5 g) in dry benzene was heated for 30 minutes. When reaction was complete, the mixture was allowed to stand in a desiccator, when a crystalline precipitate (2.9 g) quickly formed. The product was purified by recrystallization from benzene-gasoline. It formed fine colorless crystals, m.p. 108-110°, readily soluble in ether, benzene, ethyl acetate, and other solvents.

Found %: Br 16.20

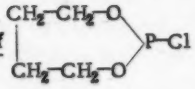
$C_{25}H_{28}O_3PBr$. Calculated %: Br 16.40

7. Action of Water on 

Ethyl ethylene phosphite (9.06 g) was placed in a small Arbuzov flask, and water (1.2 g), slightly acidified with hydrochloric acid, was added carefully. There was a vigorous reaction: the temperature of the mixture rose to 83° with formation of an apparently homogeneous solution. This was vacuum-distilled twice, yielding a colorless viscous liquid (3.5 g; b.p. 142-144°/11 mm, n_D^{20} 1.4825), which according to the results of analysis for phosphorus, was the product of the reaction of one molecule of ethyl ethylene phosphite with one molecule of water. The product was soluble in methanol, ethanol, acetone, and water, but not very soluble in ether and benzene.

Found %: P 20.53; 20.28

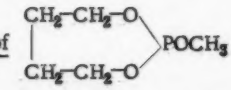
$C_4H_{11}O_4P$. Calculated %: P 20.12

8. Preparation of 

Freshly distilled phosphorus trichloride (137.42 g) was added dropwise under mechanical stirring to a mixture of 1,4-butanediol (90.08 g: 1.4 mol. equiv.), dimethylaniline (242.2 g), and dry ether (one liter). The mixture was cooled externally with snow. A precipitate of dimethylaniline hydrochloride began to appear soon after the addition of a small amount of phosphorus trichloride. When reaction was complete, the mixture was allowed to stand at room temperature for one hour. The precipitate was then filtered off and the filtrate was vacuum-distilled. As a result of four distillations (the last through a Widmer column) a product (6.1 g, 10%*) was obtained having b.p. 74-75.5°/8 mm (dec). d_0^{20} 1.2885; n_D^{20} 1.5010; found MR_D 35.55; calculated MR_D 34.81. It was a colorless liquid, which burst into flames in the air and burned with a blue flame. After being kept for three days in a sealed tube it polymerized to a colorless transparent mass, from which a yellow precipitate of phosphorus subsequently separated.

Found %: Cl 23.33

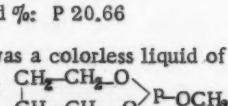
$C_4H_8O_2PCl$. Calculated %: Cl 22.88

9. Preparation of 

Methyl phosphorodichloridite (b.p. 90-92°) (61.1 g) was added to a solution of 1,4-butanediol (41.38 g) and pyridine (72.63 g) in dry ether (200 ml) (mechanical stirring, cooling with snow). The products were worked up in the usual way, and a liquid, boiling at 54-55°/4.5-5 mm, and having d_0^{20} 1.1640 and n_D^{20} 1.4642, was obtained (2 g, about 3%). MR_D: found 35.60; calculated 36.20. The greater part of the products polymerized in the distillation flask as a colorless, jellylike mass.

Found %: P 20.40

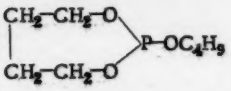
$C_5H_{11}O_3P$. Calculated %: P 20.66

The ester obtained was a colorless liquid of characteristic odor. It formed an unstable crystalline addition product with cuprous iodide:  , m.p. 142-144° (from benzene-gasoline).

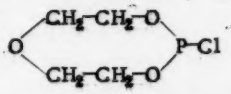
* After every distillation, there remained a large amount of red phosphorus in the distillation flask.

Found %: I 36.93

$C_5H_{11}O_3PCuI$ Calculated %: I 37.15

10. Preparation of 

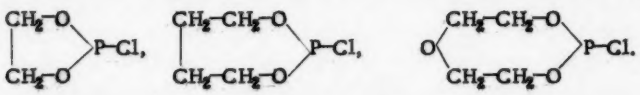
Butyl tetramethylene phosphite was prepared by a method similar to that used for the preceding ester from Menshutkin's acid chloride and the glycol in presence of pyridine. The materials taken for reaction were: $C_4H_9OPCl_2$ (24 g), 1,4-butanediol (12.35 g), and pyridine (21.66 g). Fractionation of the reaction products yielded a substance of b.p. 100-102°/9-10 mm; d_0^{20} 1.0557; n_D^{20} 1.4540; found MR_D 49.28; calculated MR_D 50.00; (2.96 g, 11%). It was a colorless liquid with a faint odor, very unstable to storage.

11. Preparation of 

This compound was prepared by a method similar to that used for the other chlorido compounds from diethylene glycol (38 g) and phosphorus trichloride (49.07 g) in presence of dimethylaniline and in a medium of dry ether (500 ml) After a number of fractionations, 3 g (5%) of a product of b.p. 104-105°/15 mm; d_0^{20} 1.2693; n_D^{20} 1.5165; found MR_D 40.14; calculated MR_D 39.43; was isolated. It was a thick oily colorless substance and was very unstable, burning spontaneously in the air with a bluish flame (compare the phosphorochloridites having a seven-membered ring).

SUMMARY

1. A study has been made of the action of ethylene glycol, of 1,4-butanediol, and of diethylene glycol on phosphorus trichloride in presence of substances that bind hydrogen chloride. Cyclic esters of phosphorochloridous acid having five-, seven-, and eight-membered rings have been synthesized:



2. By the action of alcohols on the phosphorochloridites, and also by the action of glycols on Menshutkin's acid chloride, mixed cyclic esters of phosphorous acid have been prepared; some of their properties have been studied.

Received June 23, 1952

A. M. Butlerov Chemical Research Institute
of the V. I. Ulyanov-Lenin Kazan State Univ.

LITERATURE CITED

[1] P. Carre, Bull (3), 27, 264 (1902).

[2] A. E. Arbuzov, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 2, 226 (1946).

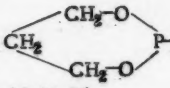
ESTERS OF "GLYCOLPHOSPHOROUS ACIDS"

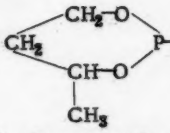
COMMUNICATION 2. COMPOUNDS HAVING A SIX-MEMBERED RING

A. E. Arbuzov and V. M. Zoroastrova

In Communication 1 [1] we have described five-, seven-, and eight-membered cyclic derivatives of phosphorous acid prepared by us from α- and γ-glycols and from diethylene glycol. In the course of investigations in this field we have studied also compounds having a six-membered ring. In the present communication we give the results of our investigations of compounds prepared from β-glycols and containing, therefore, a six-membered ring.

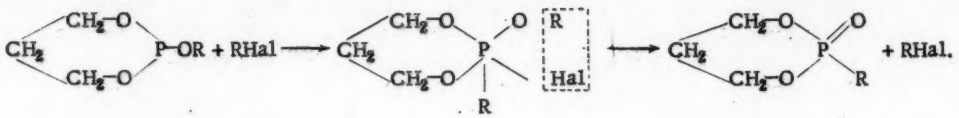
By the action of 1,3-propanediol and of 1,3-butanediol on phosphorus trichloride in presence of dimethylaniline we have obtained:

1. Trimethylene phosphorochloridite  , b.p. 70-71° at 17 mm; d_0^{20} 1.3407; n_D^{20} 1.4850; found MR_D 30.03; calculated MR_D 30.21, yield 67.5%.

2. 1-Methyltrimethylene phosphorochloridite  , b.p. 65° at 12 mm; d_0^{20} 1.2496; n_D^{20} 1.4765; found MR_D 34.91; calculated MR_D 34.81. Compound 2 was obtained in high yield (81%). It is unique in its high stability in comparison with all the other cyclic phosphorochloridites that we have studied.

By reaction with hydroxy compounds, the phosphorochloridite exchanges its halogen for a hydroxyl or methoxyl group. Reaction with alcohols in presence of substances that bind hydrogen chloride, in a medium of dry ether or other indifferent solvent, leads to ester formation. The physical properties of the resulting mixed cyclic esters of phosphorous acid are given in Table 1.

When they react with alkyl halides, these six-membered cyclic esters undergo isomerization: the ring remains intact, and cyclic esters of alkylphosphonic acids are formed. The reaction is represented by A. E. Arbuzov's scheme:



The isomerization products are given in Table 2.

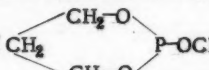
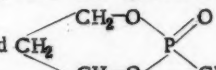
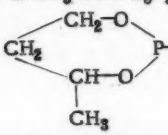
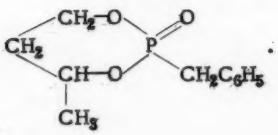
When reaction occurs with benzyl chloride or bromide, the ring of the ester again remains intact. Reaction of  with $C_6H_5CH_2Cl$ yields the compound  ; b.p. 138-139°. By the action on  (where R = CH_3, C_2H_5, C_4H_9) of benzyl chloride or bromide, a product of m.p. 120-121° is formed; the analytical results correspond to  .

TABLE 1

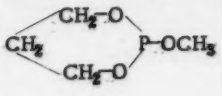
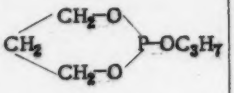
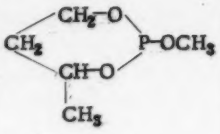
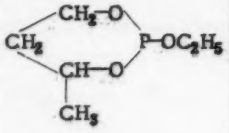
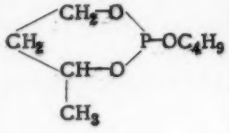
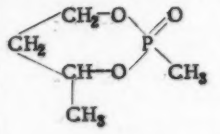
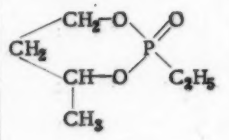
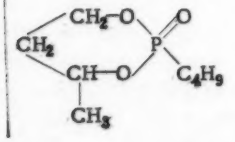
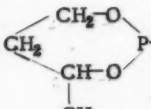
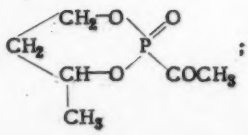
No.	Formula	B.p. °C	Pressure (mm Hg)	d_0^{20}	n_D^{20}	MR_D found	MR_D calculated
1		65-66 (50-51)	23 11	1.1758	1.4465	31.46	31.59
2		69	9	1.0582	1.4452	41.29	40.77
3		62	13	1.1092	1.4420	35.80	36.15
4		63-64	8	1.0696	1.4410	40.51	40.77
5		75-76	3.5-4	1.0252	1.4472	50.00	50.01

TABLE 2

No.	Formula	B.p. °C	Pressure (mm Hg)	d_0^{20}	n_D^{20}	MR_D found	MR_D calculated
1		117-119	7	1.2031	1.4500	33.52	33.44
2		123	5	1.1541	1.4510	38.29	38.06
3		127	5	1.1039	1.4538	47.11	47.25

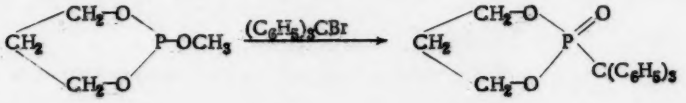
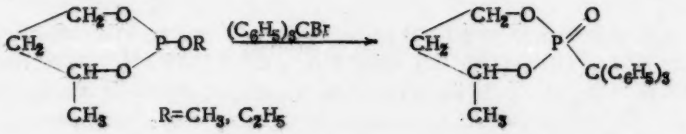
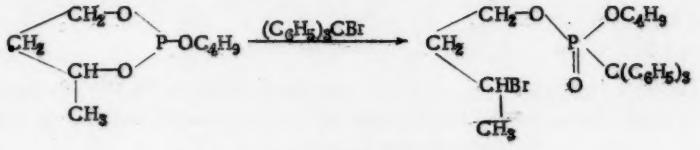
An interesting result was obtained in the study of the reaction of the esters with bromotriphenylmethane. By reaction with $(C_6H_5)_3CBr$, methyl (or ethyl) trimethylene (or 1-methyltrimethylene) phosphite yielded esters of triphenylmethylphosphonic acid. Butyl 1-methyltrimethylene phosphite reacted with the same compound with opening of the ring (Table 3).

The methyl ester  reacted with acetyl bromide, giving a satisfactory yield of a cyclic ester of acetylphosphonic acid  ; b.p. 142-143° at 4-3.5 mm; d_0^{20} 1.2574; n_D^{20}

1.4555; found MR_D 38.20; calculated MR_D 38.10.

The action of water on the esters was tried, and it was found that reaction proceeds with preservation of the ring, leading to formation of cyclic acids. The ring remains intact also when the phosphorochloridites react with water.

TABLE 3

No.	Formula	B.p. °C
1		228-229
2		192-193
3		109-110

EXPERIMENTAL

1. Preparation of Trimethylene Phosphorochloridite

The materials taken for recreation were 1,3-propanediol (100 g), phosphorus trichloride (180.6 g), and dimethylaniline (318.4 g). Since 1,3-propanediol is of low solubility in ether, the reaction was carried out in a mixture of dry dioxane and dry ether. The 1,3-propanediol and dimethylaniline were dissolved in a 1:1 mixture of dioxane and ether (700 ml), and before commencing the reaction a few crystals of dimethylaniline hydrochloride were added to the solution. Freshly distilled phosphorus trichloride (180.6 g) was added dropwise to the solution, which was cooled with snow. The filtrate, after removal of the precipitated dimethylaniline hydrochloride, was fractionated through a Widmer column, yielding a product (124 g, 67.5 %) boiling at 70-71°/17 mm, and having d_0^{20} 1.3407; n_D^{20} 1,4850; found MR_D 30.03; calculated MR_D 30.21. It is a colorless oily liquid that fumes in air.

Found %: P 22.21

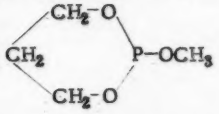
$C_3H_6O_2PCl$. Calculated %: P 22.06

2. Preparation of 1-Methyltrimethylene Phosphorochloridite

A mixture of 1,3-butanediol (90 g), dimethylaniline (242.5 g), and dry ether (one liter) was introduced into a two-liter round-bottomed flask fitted with reflux condenser and mechanical stirrer. The reaction mixture was cooled with water containing snow. Freshly distilled phosphorus trichloride (137.42 g), diluted with an equal volume of dry ether, was added dropwise under constant stirring. When reaction was complete, the dimethylaniline hydrochloride was filtered off and washed three or four times with dry ether. The product, after removal of the ether, was vacuum-distilled from an Arbuzov flask. After a second distillation, a product (125 g, 81%) was obtained boiling at 65°/12mm, having the following constants: d_0^{20} 1,2496; n_D^{20} 1.4765; found MR_D 34.91; calculated MR_D 34.81. It is a colorless oily liquid, soluble in organic solvents. It fumes in air, but can be preserved unchanged in a sealed tube.

Found %: Cl 22.71

$C_4H_8O_2PCl$. Calculated %: Cl 22.81

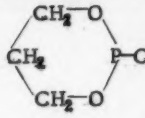
3. Preparation of 

Trimethylene phosphorochloridite (63.2 g) was added to a mechanically stirred solution of absolute

methanol (12.4 g) and anhydrous pyridine (35.55 g) in dry ether (150 ml) contained in a flask that was cooled externally with snow. With the first few drops of the phosphorochloridite a crystalline precipitate of pyridine hydrochloride began to appear. When reaction was complete, the pyridine hydrochloride was filtered off and the filtrate was vacuum-distilled. After a second distillation, a liquid (45.6 g, 61.2%) was obtained having B.p. 65-66° at 23 mm (50-51° at 11 mm) 45.6 g, or 61.2% of theory: d_0^{20} 1.1758; n_D^{20} 1.4465; found MR_D 31.46; calculated MR_D 31.59.

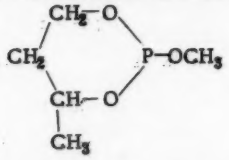
Found %: P 22.78
$C_4H_9O_3P$. Calculated %: P 22.79

4. Preparation of Propyl Trimethylene Phosphite

The compound was prepared by a method similar to that used for the previous compound from the phosphorochloridite  (22.8 g), propyl alcohol (9.72 g), and pyridine (12.82 g) in a medium of dry ether (200 ml). The product (12 g 45%) b.p. 69°at 9 mm; d_0^{20} 1.0582; n_D^{20} 1.4452; found MR_D 41.29; calculated MR_D 40.77. It was a colorless oily liquid, soluble in organic solvents. It reacted with cuprous halides with evolution of heat (we did not succeed in isolating crystalline products).

Found %: P 18.51
$C_6H_{13}O_3P$. Calculated %: P 18.90

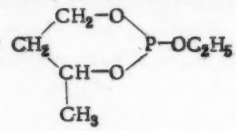
In addition to the product of b.p. 69°/9 mm, 2 g of a fraction boiling at 168-169°/12 mm (n_D^{20} 1.4625; d_0^{20} 1.2231), was isolated. Attempts to determine its structure were not successful (analysis for phosphorus gave 23.33% P).

5. Preparation of the Ester 

A mixture of absolute methanol (12.7 g), pyridine (31.85 g), and dry ether (300 ml) was cooled to 5°. The phosphorochloridite (61.3 g), diluted with an equal amount of dry ether, was added to the solution (mechanical stirring and cooling with snow). The reaction continued for 1 hour 30 minutes, and the mixture was then allowed to stand at room temperature for 30 minutes, after which pyridine hydrochloride was filtered off. Vacuum fractionation of the filtrate from an Arbuzov flask yielded a product (37.7 g, 60%) having b.p. 62°/13 mm, d_0^{20} 1.1092; n_D^{20} 1.4420; found MR_D 35.80; calculated MR_D 36.15. It was a colorless liquid having an unpleasant odor similar to that of trimethyl phosphite.

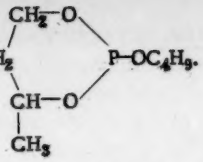
Found %: P 20.40
$C_5H_{11}O_3P$. Calculated %: P 20.66

The same ester (b.p. 64° at 16 mm; n_D^{20} 1.4422) was obtained by reaction in ether solution of CH_3OPCl_2 with 1,3-butanediol in presence of pyridine, but the yield was lower (37.3%).

6. Preparation of the Ester 

The phosphorochloridite (50 g), diluted with an equal volume of dry ether, was added dropwise to a cooled (to 5°) mixture of absolute ethanol (14.88 g), pyridine (25.64 g), and dry ether (250 ml). When reaction was complete, the flask was allowed to stand for 30 minutes at room temperature; the pyridine salt was then filtered off, and the filtrate was vacuum-distilled from an Arbuzov flask. After a second distillation a product (40.65 g, 76.5%) was obtained having b.p. 63-64° at 8 mm; d_0^{20} 1.0696; n_D^{20} 1.4410; found MR_D 40.51; calculated MR_D 40.77. It was a colorless, transparent liquid of characteristic odor, soluble in ether, benzene, and chloroform. It reacted with cuprous halides (with CuI it yielded a crystalline product, m.p. 135° (from absolute alcohol). It reacted vigorously with water that had been slightly acidified with hydrochloric acid.

Found %: P 18.70; 18.60
$C_6H_{13}O_3P$. Calculated %: P 18.90.

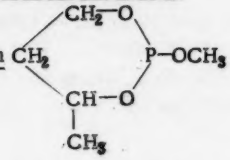
7. Preparation of  .

Butyl 1-methyltrimethylene phosphite was prepared from Menshutkin's acid chloride and 1,3-butanediol in presence of dimethylaniline. A solution of 1,3-butanediol (52.65 g) and dimethylaniline (144.8 g) in a mixture of dry benzene (700 ml) and anhydrous dioxane (150 ml) was cooled with snow (before the beginning of the reaction, about 1 g of dimethylaniline hydrochloride was introduced). Butyl phosphorodichloridite (101.7 g) was added dropwise to this solution. The reaction products were worked up in the usual way, and the butyl ester obtained (60.4 g, 54.1%) had b.p. 75-76° at 3.5-4mm; d_0^{20} 1.0252; n_D^{20} 1.4472; found MR_D 50.00; calculated MR_D 50.01. It was a colorless oily liquid, more viscous than the preceding esters, and having an odor characteristic of butyl esters.

Found %: P 15.99; 16.16

$C_8H_{17}O_3P$. Calculated %: P 16.13

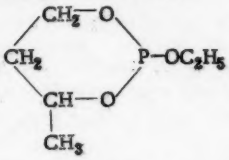
8. Action of Alkyl Halides on the Esters

1. Action of methyl iodide on 

The methyl ester (10.9 g) and methyl iodide (10.31 g) were sealed in a tube (slight warming up was observed). The mixture was heated at 100° for two hours. After methyl iodide (about 6 g) had been driven off, the products were vacuum-distilled twice. A substance (6 g, 58%) was obtained having b.p. 117-119° at 7 mm; d_0^{20} 1.2031; n_D^{20} 1.4500; found MR_D 33.52; calculated MR_D 33.44. It was a colorless oily substance, more viscous than the original methyl ester, and practically without odor. It was soluble in alcohol, ether, benzene and water.

Found %: C 39.49; 39.58; H 7.28; 7.48

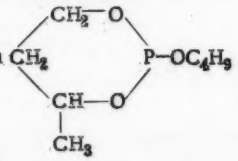
$C_5H_{11}O_3P$. Calculated %: C 39.97; H 7.38

2. Action of ethyl iodide on 

The ethyl ester (12 g) and ethyl iodide (11.45 g) were sealed in a tube (no reaction was to be observed at ordinary temperature). The tube was heated in a boiling water bath for five hours. Fractionation of the reaction products gave ethyl iodide (10 g) and a product (5 g, 41.7%) having b.p. 123° at 5 mm; d_0^{20} 1.1541; n_D^{20} 1.4520; found MR_D 38.29: Calculated MR_D 38.01.

Found %: C 43.39; H 7.99

$C_6H_{13}O_3P$. Calculated %: C 43.87; H 7.98

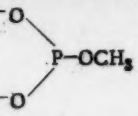
3. Action of butyl bromide on 

Butyl 1-methyltrimethylene phosphite (14 g) and butyl bromide (10.4 g) were heated in a sealed tube at 150-160° for 5 hours 30 minutes. After a number of vacuum distillations, a product (4.5 g, 32.1%) was obtained having b.p. 127° at 5 mm; d_0^{20} 1.1039; n_D^{20} 1.4538; found MR_D 47.11; calculated MR_D 47.25.

Found %: P 15.82; 15.85

$C_8H_{17}O_3P$. Calculated %: P 16.13

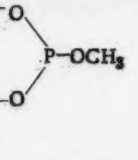
9. Action of Bromotriphenylmethane on the Esters

1. Action of $(C_6H_5)_3CBr$ on 

A solution of methyl trimethylene phosphite (0.68 g) and bromotriphenylmethane (1.5 g) in benzene (3 ml) was boiled for 20 minutes. The reaction mixture crystallized out when half of the benzene had been driven off. The product was purified by recrystallization from dioxane; it had m.p. 227-228°.

Found %: C 72.12; H 5.80; P 8.70

$C_{22}H_{21}O_3P$. Calculated %: C 72.49; H 5.81; P 8.51

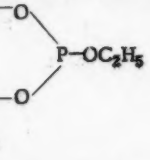
2. Action of $(C_6H_5)_3CBr$ on 

The methyl ester (0.75 g), bromotriphenylmethane (0.61 g), and dry benzene (4 ml) were placed in a 5-ml Arbuzov flask, and the mixture was boiled cautiously for 30 minutes. Part of the benzene was driven off, and 3-4 ml of gasoline was added. The mixture was cooled with snow, and a fine crystalline precipitate was formed. The product melted, after recrystallization from a benzene-gasoline mixture, at 192-193°. It was similar to the preceding product in properties.

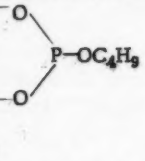
Found %: C 72.30; H 6.06; P 8.61

$C_{23}H_{23}O_3P$. Calculated %: C 72.97; H 6.12; P 8.20

Hydrolysis of product of m.p. 192-193°: The product (0.2 g) and 20% hydrochloric acid (5 ml) were heated in a sealed tube at 180° for five hours. Crystals of triphenylmethylphosphonic acid (m.p. 276-279°) were obtained.

3. Action of $(C_6H_5)_3CBr$ on 

A mixture of the ethyl ester (0.82 g), bromotriphenylmethane (1.5 g), and dry benzene (5 ml) was heated in an Arbuzov flask for 45 minutes. The reaction products were worked up as before and yielded a small amount of crystals of m.p. 192-193°. In admixture with the preceding product it melted without depression.

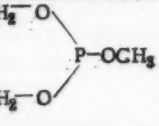
4. Action of $(C_6H_5)CBr$ on 

For the reaction 1.99 g of the butyl ester and 3.23 g of bromotriphenylmethane were taken. The benzene solution was heated for 20 minutes, and gasoline (5 ml) was then added. A halogen-containing product of m.p. ~110° was obtained.

Found %: P 6.28; Br 15.58

$C_{27}H_{32}O_3PBr$. Calculated %: P 6.01; Br 15.51

10. Action of Benzyl Chloride and Bromide on the Esters

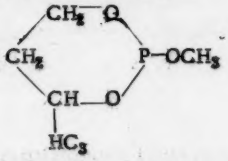
1. Action of $C_6H_5CH_2Cl$ on 

Methyl trimethylene phosphite (6.6 g) and benzyl chloride (6.1 g) were heated in a sealed tube at 100°

for 3 hours 30 minutes. The reaction did not go to completion (the odor of the original ester persisted). Heating was continued at 140-150° for four hours. When the tube was opened, vigorous frothing, due to the evolution of methyl chloride, occurred. The reaction product rapidly crystallized out, yielding a compact mass. After recrystallization from benzene, the substance melted at 138-139°.

Found %: C 56.20; H 5.93; P 14.65

$C_{10}H_{15}O_3P$. Calculated %: C 56.57; H 6.17; P 14.62

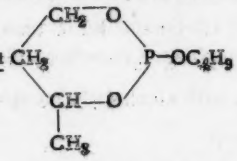
2. Action of benzyl chloride on 

A mixture of the ester (7.3 g) and benzyl chloride (6.2 g) was heated in a sealed tube at 140° for four hours. By fractionation of the products, a fraction (4 g) of b.p. 168-193°/3-4 mm was obtained. On standing, it yielded colorless crystals, which, after recrystallization from benzene, melted at 120-121°. They were colorless needles, soluble in benzene and in alcohol, poorly soluble in ether and in ligroin.

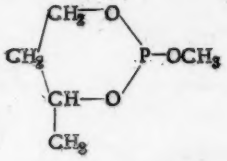
Found %: P 13.97

$C_{11}H_{15}O_3P$. Calculated %: P 13.71

Rast molecular weight estimation: M (found) 231.1 (calculated for $C_{11}H_{15}O_3P$: 226.14).

3. Action of benzyl bromide on 

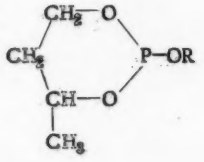
Butyl 1-methyltrimethylene phosphite (2.6 g) and benzyl bromide (2.4 g) were heated in a sealed tube at 150-155° for four hours. When the tube was opened there was no odor of the original ester or of benzyl bromide. After standing overnight, the product partly crystallized out. The crystals (0.6 g, 21%) melted, after recrystallization from benzene, at 120-120.5°. In admixture with the preceding product it melted without depression.

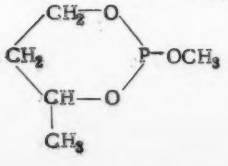
11. Action of Acetyl Bromide on 

An ethereal solution of acetyl bromide (3.5 g) was added dropwise to a solution of methyl 1-methyltrimethylene phosphite (4.1 g) in dry ether (5 ml) contained in a small Arbuzov flask, which was cooled with snow. The temperature within the mixture did not exceed 8°. Solvent was driven off, and the reaction products were vacuum-distilled. A fraction (2.3 g, 47.3%) was isolated having b.p. 142-143° at 3-3.5 mm; d_0^{20} 1.2574; n_D^{20} 1.4555; found MR_D 38.20; calculated MR_D 38.10. It was an oily liquid having a faint odor. It dissolved in organic solvents and in water.

Found %: P 17.04

$C_6H_{11}O_6P$. Calculated %: P 17.40

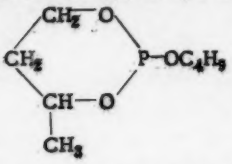
12. Action of Water on the Ester 

1. Action of Water on 

To 5.6 g of the methyl ester 0.67 g (one mole per mole of ester) of water was added (the water was slightly acidified with hydrochloric acid). The temperature of the mixture rose immediately to 97°. Vacuum fractionation yielded a fraction (2 g, 40%) of b.p. 150-155°/10-11 mm, and this rapidly crystallized out. The product was recrystallized from gasoline (m.p. 48-50°).

Found %: C 35.00; H 6.89; P 22.7

$C_4H_9O_3P$. Calculated %: C 35.27; H 6.66; P 27.79

2. Action of water on 

Slightly acidified water (0.36 g) was added to butyl 1-methyltrimethylene phosphite (3.84 g). Reaction did not begin at once: at first an emulsion was formed, and the ester did not appear to react. After some time the mixture was warmed, and a clear homogeneous solution was formed. In the distillation of the products butyl alcohol was detected. Crystals of a cyclic acid, m.p. 48-50°, were obtained. The silver salt (decomposition temperature 220°) was prepared:

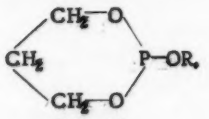
Found %: Ag 44.66

$C_4H_8O_3PAg$. Calculated %: Ag 44.40

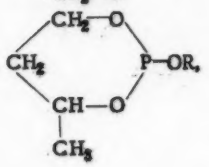
SUMMARY

1. By the action of 1,3-propanediol and of 1,3-butanediol on phosphorus trichloride, the cyclic compounds, trimethylene phosphorochloridite and 1-methyltrimethylene phosphorochloridite, have been prepared.

2. By reaction of the phosphorochloridites with alcohols in presence of dimethylaniline, the following mixed esters have been synthesized:



where R = CH_3, C_3H_7;



where R = CH_3, C_2H_5, C_3H_7.

Some of their properties have been studied.

LITERATURE CITED

[1] A. E. Arbuzov and V. M. Zoroastrova, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., No. 5, 770 (1952).*

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* See Consultants Bureau translation, p.697.

N-SUBSTITUTED CYCLIC ESTERS OF PHOSPHORAMIDOUS ACID

A. E. Arbuzov and V. M. Zoroastrova

The present work represents a development of our investigations of cyclic esters of phosphorous acid. We found in 1946 [1] that phosphorous trichloride reacts with glycols in presence of pyridine or dimethylaniline with formation of cyclic esters of phosphorochloridous acid. In this way we have synthesized, in the last few years, esters of phosphorochloridous acid having five-, six-, seven-, and eight-membered rings derived from α-, β-, and γ-glycols, and from diethylene glycol [2]. The phosphorochloridites are colorless fuming liquids, and are very reactive. Those having seven- and eight-membered rings ignite spontaneously in air and burn with a blue flame; they tend to polymerize. The phosphorochloridites react with anhydrous alcohols in presence of dimethylaniline or pyridine, giving mixed cyclic esters of phosphorous acid, which also are very reactive compounds having interesting characteristics.

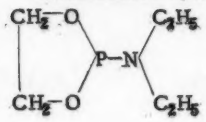
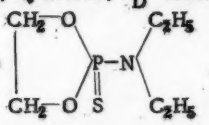
In the present work we have studied the reactions of phosphorochloridites derived from α- and β-glycols with certain aliphatic and aromatic amines: dimethylamine, diethylamine, piperidine, aniline, and methylaniline.

By the action of these amines on the phosphorochloridites, we have synthesized a number of N-substituted cyclic esters of phosphoramidous acid. which contain tervalent nitrogen as well as tervalent phosphorus. The physical properties of the compounds obtained are presented in Table 1.

The first seven compounds listed in Table 1 were prepared by introducing 1 mole of cyclic phosphorochloridite into an ether or benzene solution of 2 moles of amine*. The hydrogen chloride formed was taken up by the second molecule of amine and was separated from the reaction product as amine hydrochloride. The solvent was driven off, and the product was vacuum-distilled. Yields of N-substituted cyclic esters of phosphoramidous acid varied from 55 to 73%. The seven compounds are all colorless liquids, similar in appearance to the previously studied mixed cyclic esters of phosphorous acid, and having a faint but characteristic odor.

Compounds 8 and 9, which have aromatic radicals on the nitrogen, are very viscous liquids, also having characteristic odors. They were prepared by the action of aromatic amines on the phosphorochloridite in presence of metallic sodium. Yields did not exceed 22.8%.

All the synthesized N-substituted cyclic esters of phosphoramidous acid, like the full esters of phosphorous acid, react with cuprous halides. In this case also, the reaction proceeds with considerable evolution of heat. Some of the compounds formed with cuprous chloride, with cuprous bromide, and with cuprous iodide were prepared in a crystalline form (Table 2).

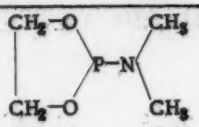
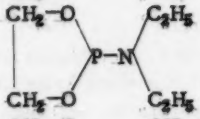
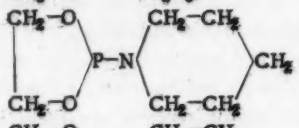
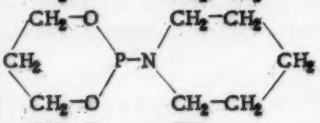
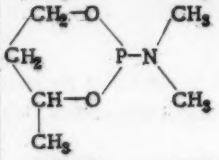
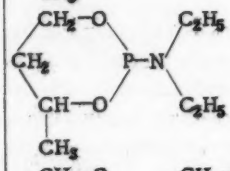
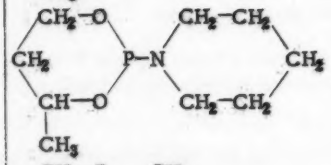
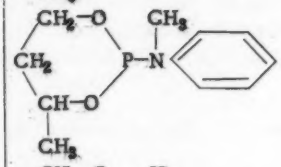
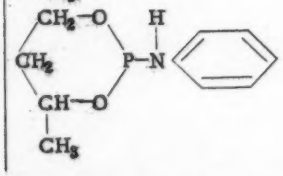
N-substituted cyclic esters of phosphoramidous acid are able to unite with sulfur. By the action of sulfur on  , a product (b.p. 133-134.5* at 3 mm; d_0^{20} 1.1825, n_D^{20} 1.5050), was isolated in a pure form; it corresponded in analysis to  .

The products of the reaction of other N-substituted phosphoramidites with sulfur could not be obtained in a pure state since they were largely decomposed when distilled.

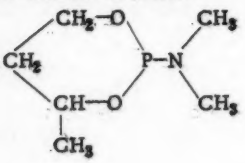
Alkyl halides also react with the nitrogen-containing esters, but the reaction is complex, and we did not

* After we had finished our investigation, there appeared a paper by H. J. Lucas, F. W. Mitchell, and C. N. Scully, "Cyclic Phosphites of some Aliphatic Glycols" (J. Am. Chem. Soc., 72, 5491 (1950), in which Compounds 2 and 3 (Table 1) are described. The value of MR_D for Compound 3 is given incorrectly in this paper.

TABLE 1

No.	Formula	B.p. (°C)	Pressure (mm Hg)	d_0^{20}	n_D^{20}	MR_D Found	MR_D Calculated
1		61-62	11	1.1285	1.4730	33.58	33.88
2		66-67	3.5	1.0639	1.4680	42.61	43.08
3		89-90	2.5-3	1.1454	1.5040	45.27	45.49
4		96-97	4	1.1173	1.5020	50.01	50.16
5		71	13.5	1.0423	1.4650	43.26	43.12
6		69-70	2	1.0050	1.4620	52.36	52.38
7		95-96	3	1.0741	1.4930	54.95	54.77
8		133-134	3	1.1382	1.5442	62.65	62.60
9		136-137	2	1.1748	1.5558	57.84	57.93

succeed in isolating any homogeneous substances from the mixture of products. It is probable that the reaction results in rupture of the P–N link.

By the action of water (slightly acidified with hydrochloric acid) on the compounds 

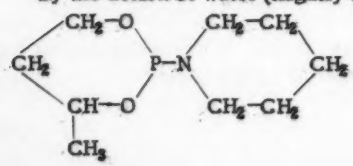
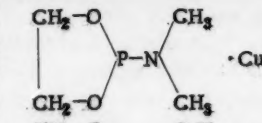
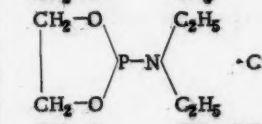
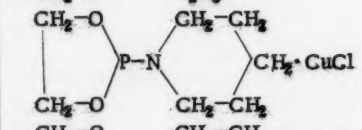
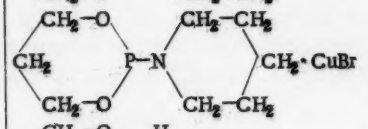
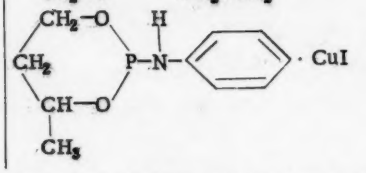
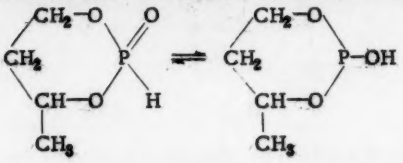
and 

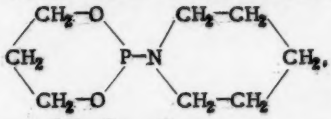
TABLE 2

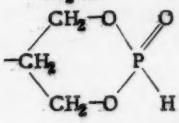
No.	Formula	M.p. (° C)
1		108-109
2		108
3		128-130
4		167-167.5
5		134-138

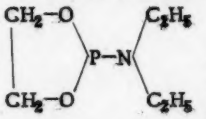
we isolated, in a pure state, the cyclic acid



(m.p. 48-50°), which was previously obtained by us by the hydrolysis of mixed cyclic esters; by the action of acidified water on

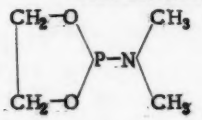
 , we obtained

 in a less pure form.

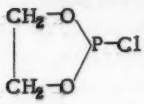
By the action of hydrogen on a solution of  in ether we obtained a product that corresponded in analysis to the product of the addition of one atom of oxygen to one molecule of ethylene N,N-diethylphosphoramidite. The structure of this oxidation product was not investigated further.

EXPERIMENTAL

1. Preparation of the Ester



Dimethylamine (13 g) and dry benzene (150 ml) were placed in a flask fitted with reflux condenser and mechanical stirrer. The flask was cooled externally with water containing snow. The phosphorochloridite



(15 g), diluted with dry benzene (20 ml), was added from a dropping funnel. When reaction was complete, the precipitate of dimethylamine hydrochloride was filtered off and washed two or three times with dry benzene. The filtrate was vacuum-fractionated from an Arbuzov flask. After two fractionations, the following fractions were separated:

Fraction I, B.p. 60 - 61° at 12 mm; 1.2 g; n_D^{20} 1.4735
Fraction II, B.p. 61 - 62° at 11 mm; 11.6 g (yield 73%); n_D^{20} 1.4730
Fraction III, B.p. 62 - 63.5° at 11 mm; 0.5 g; n_D^{20} 1.4728

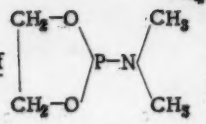
Fraction II was investigated in greater detail: d_0^{20} 1.1285; d_0^0 1.1487; n_D^{20} 1.4730. Found MR_D 33.58; calculated MR_D 33.88.

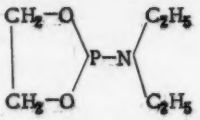
Found %: P 22.84; N 10.61
$C_4H_{10}O_2PN$. Calculated %: P 22.94; N 10.36

Fraction II was a mobile oily liquid having an unpleasant odor reminiscent of the odor of trimethyl phosphite. It was soluble in ether, benzene, chloroform, and other organic solvents; it reacted vigorously with water; and with cuprous halides it gave crystalline complex compounds, which decomposed rapidly in air. Thus, when CuCl (0.5 g) was added to the ester (0.75 g), the temperature of the mixture rose to 49° and the whole mass rapidly crystallized. However, when attempts were made to recrystallize the product from benzene, it decomposed. By reaction in a similar way of equimolecular proportions of ester and cuprous iodide, a product of m.p. 108-109° (from butyl acetate) was obtained. Analysis for iodine gave the following results:

Found %: I 38.81

$C_4H_{10}O_2PNCuI$. Calculated %: I 38.98

Reaction of  with methyl iodide. Methyl iodide (7.1 g) was added to the ester (6.6 g, i.e., one mole per mole of methyl iodide). The mixture immediately became milky, and its temperature rose to 103° and higher. The contents of the tube started to boil, and the greater part of them were ejected. The remaining part consisted of a thick red mass, and attempts to isolate definite products from this by vacuum distillation were not successful.

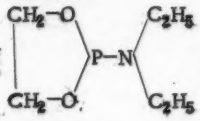
2. Preparation of the Ester 

The materials taken for reaction were: ethylene phosphorochloridite (35.44 g), diethylamine (41 g), and dry ether (200 ml). The phosphorochloridite, diluted with an equal amount of ether, was added dropwise to the mechanically stirred ethereal solution of the amine. When reaction was complete, the reaction mixture was heated on a water bath for one hour. After the usual treatment, the reaction products were vacuum-distilled from an Arbuzov flask. After three distillations a product (30 g, 65.9%) having b.p. 66-67°/3.5 mm, d_0^{20} 1.0639; n_D^{20} 1.4680; found MR_D 42.61; calculated MR_D 43.08, was obtained.

Found %: P 19.33; 19.23; N 8.77

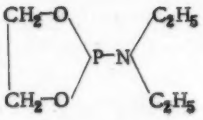
$C_6H_{14}O_2PN$. Calculated %: P 19.00; N 8.58

It was a colorless oil of characteristic odor. Oxidation of this or the preceding ester with nitric acid was accompanied by deflagration.

Reaction of  with CuCl and with CuBr. 1) When the ester (1.63 g) and cuprous chloride (0.99 g) were mixed, the temperature rose to 53°. A thick mass, soluble in ether, benzene and chloroform, was formed; attempts to crystallize it failed. 2) The ester (0.81 g) and CuBr (0.71 g) yielded a colorless crystalline substance, which, after two crystallizations from benzene-gasoline, melted at 108°. It was unstable in air.

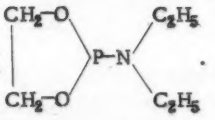
Found %: Br 25.73; P 10.33

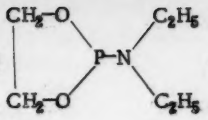
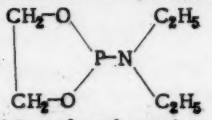
$C_6H_{14}O_2PNCuBr$. Calculated %: Br 26.06; P 10.11

Addition of sulfur to the ester  . Finely divided crystalline sulfur (1 g) was added to the cooled ester (5 g, i.e. one mole per mole of sulfur), contained in a small Arbuzov flask. A highly exothermic reaction occurred, and the sulfur dissolved in the ester with formation of a homogeneous colorless solution. The solution was vacuum-distilled yielding a product (3 g) of b.p. 133-134.5°/3 mm (with some decomposition) (d_0^{20} 1.1825; n_D^{20} 1.5050; found MR_D 48.92; calculated MR_D 48.51.) It was a viscous liquid of faint odor.

Found %: P 16.14; S 16.92

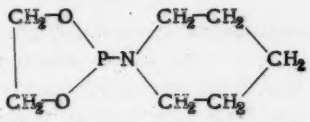
$C_6H_{14}O_2PNS$. Calculated %: P 15.83; S 16.43

Action of C_2H_5I on the ester  . A mixture of the ester (10.62 g) and ethyl iodide (10.2 g, i.e., one mole per mole of ester) was allowed to stand in a sealed tube at room temperature for five days. When the tube was opened, there was no odor of the original ester. The contents consisted of a fairly thick, colorless liquid. By distillation at ordinary pressure on the water bath, 5 g of ethyl iodide was driven off. When the mixture was heated more strongly, a very vigorous reaction set in with evolution of gaseous products; it lasted for 2-3 minutes. The contents of the flask became dark red. A small amount of dark-red liquid was driven off at 110-112° under 2.5-5.5 mm pressure, and a large residue of viscous liquid remained in the flask. The experiment was repeated several times, always with the same result: it was not found possible to isolate any product in the pure state.

Action of hydrogen peroxide on  . To a solution of hydrogen peroxide (2.5 g of 100%) in dry ether (100 ml),  (10 g) was added in three portions, the reaction flask being cooled with snow. With the addition of each portion of the ester, a vigorous reaction occurred and the reaction mixture boiled. The reaction products were distilled, and a fraction (4.2 g, 38.5%) of b.p. 132°/5.5-6 mm was separated. It was a colorless odorless liquid, soluble in organic solvents and in water and having the following constants: d_0^{20} 1.1735; n_D^{20} 1.4522; calculated MR_D 41.95; found MR_D 41.18.

Found %: P 17.27

$C_6H_{14}O_3PN$. Calculated %: P 17.30

3. Preparation of the ester 

The phosphorochloridite (20 g) was added to a mechanically stirred solution of piperidine (27 g) in ether (100 ml). The mixture was heated for one hour on the water bath and was then cooled to room temperature. The precipitate of piperidine hydrochloride was filtered off, and the filtrate was vacuum-distilled twice. A product (19 g, 68.5%) was obtained that boiled at 89-90° under 2.5-3 mm pressure and had d_0^{20} 1.1454; n_D^{20} 1.5040; found MR_D 45.27; calculated MR_D 45.49.

Found %: P 17.53; N 8.16

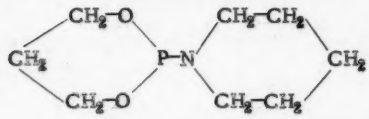
$C_7H_{16}O_2PN$. Calculated %: P 17.70; N 7.99

The product was more viscous than the previous esters.

Compound with cuprous chloride. By reaction in equimolecular proportions of the ester with CuCl, a crystalline substance was obtained. It was recrystallized several times from benzene-gasoline (m.p. 128-130°). The crystals were colorless, but rapidly yellowed in air.

Found %: Cl 12.79

$C_7H_{16}O_2PNCuCl$. Calculated %: Cl 12.92

4. Preparation of the Ester 

The phosphorochloridite, diluted with an equal volume of dry ether, was added to a mechanically stirred solution of piperidine (20 g) in dry ether (120 ml). As soon as the first drops of phosphorochloridite had been added, a white crystalline precipitate of piperidine hydrochloride began to appear. When the whole of the phosphorochloridite had been added, the reaction mixture was heated on the water bath for 30 minutes. Vacuum distillation yielded a product (14 g, 65%) of b.p. 96-97°/4 mm, d_0^{20} 1.1173; n_D^{20} 1.5020; found MR_D 50.01; calculated MR_D 50.11; a colorless oil having an odor similar to that of the preceding piperidine compound.

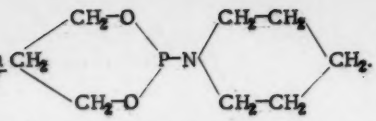
Found %: N 7.8

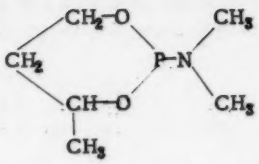
$C_8H_{16}O_2PN$. Calculated %: N 7.4

Compound with cuprous bromide. CuBr (0.71 g) was added to the ester (0.95 g). The temperature of the mixture rose to 78°, and a homogeneous mass was formed which rapidly crystallized. The product, after recrystallization from butyl acetate, formed colorless glistening crystals, m.p. 167-167.5°.

Found %: Br 24.05

$C_8H_{16}O_2PNCuBr$. Calculated %: Br 24.02

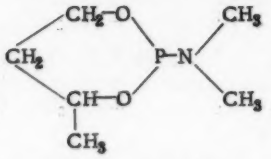
Action of water on  . Water (0.66 g), slightly acidified with hydrochloric acid, was added to an equimolecular proportion of the ester (7 g), contained in a small Arbuzov flask. After some time, the emulsion that was at first formed was converted into a homogeneous solution, and the temperature rose to 46°. Vacuum distillation yielded a fraction of b.p. 143-144°/4 mm; n_D^{20} 1.4658.; a colorless, very viscous liquid, soluble in water, alcohol, benzene, and dioxane, but not soluble in ether.

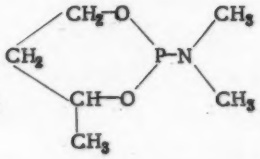
5. Preparation of the Ester 

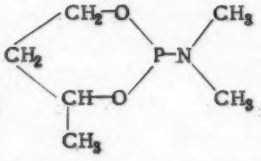
1-Methyltrimethylene phosphorochloridite was added to a cooled, mechanically stirred solution of dimethylamine (11 g) in dry ether (120 ml). When all the phosphorochloridite had been added, dimethylamine hydrochloride was filtered off, and the filtrate was vacuum-distilled from an Arbuzov flask having two bulbs. After redistillation, a product (11.51 g, 57.8%) was obtained having b.p. 71° at 13.5 mm; d_0^{20} 1.0423; n_D^{20} 1.4650; found MR_D 43.26; calculated MR_D 43.12.

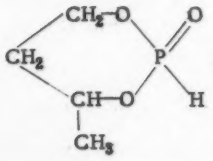
Found %: P 19.00

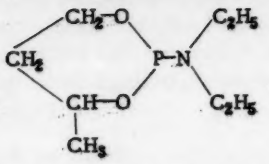
$C_6H_{14}O_2PN$. Calculated %: P 19.00

Action of methyl iodide on  . Methyl iodide (3.6 g) was added to the ester (4.2 g), which was cooled with snow. A very violent reaction occurred, and a part of the mixture was thrown out of the reaction flask. A viscous liquid was obtained. Vacuum distillation yielded 3-4 drops of a fraction of b.p. 57-62°/3 mm. The residue did not distil (bath temperature 200-220°); it was a thick greasy liquid of unpleasant odor.

Action of $C_6H_5CH_2Br$ on  . The ester (2 g) was mixed with benzyl bromide (2.08 g). The temperature of the mixture rose very slowly and remained at 30-36° for 30 minutes. The whole of the benzyl bromide reacted. The reaction products were allowed to stand for two hours at room temperature and then were vacuum-distilled. A fraction (1.1 g) of b.p. 73-112°/3 mm was obtained (bath temperature 220°). The remaining part (1.8 g) was a solid glasslike product, insoluble in organic solvents and in water.

Action of water on  . Water, (0.36 g) slightly acidified with hydrochloric acid, was added to the ester (3 g), contained in a small Arbuzov flask. On being shaken, the mixture at first formed an emulsion, and then reaction set in with rise in temperature to 45° and the appearance of the odor of dimethylamine. Distillation yielded a product (1 g) of b.p. 138°/3.5 mm, which crystallized when seeded with crystals of the previously prepared cyclic acid:

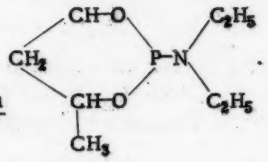
 ; m.p. 48-49°.

6. Preparation of the Ester 

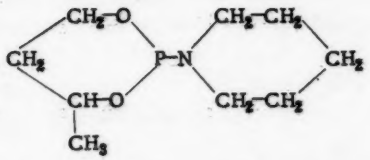
This compound was obtained in analogous fashion from 1-methyltrimethylene phosphorochloridite (18.7 g) and diethylamine (17.7 g) in a medium of dry ether. After the usual treatment of the reaction products and two vacuum fractionations, a fraction (12.8 g, 55.3%) was obtained having b.p. 69-70°/2 mm; d_0^{20} 1.0050; n_D^{20} 1.4625; found MR_D 52.38; calculated MR_D 52.36.

Found %: P 16.21; 16.10; N 7.56

$C_8H_{18}O_2PN$. Calculated %: P 16.21; N 7.32

Action of ethyl bromide on 

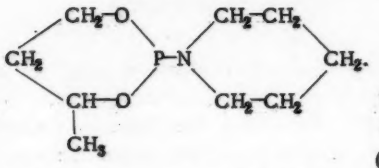
A mixture of the ester (8.8 g) and ethyl bromide (5 g) was heated in a sealed tube having a drawn-out portion. Heating was at 50-55° for six hours, at 70-80° for four hours, and at 90° for three hours. No further change in volume was then observed. On being vacuum-distilled, the reaction products were largely decomposed; it was not possible to isolate any individual substances.

7. Preparation of the Ester 

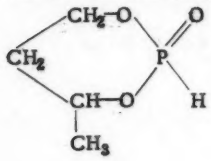
The phosphorochloridite (25.6 g), diluted with an equal amount of ether, was added to a mechanically stirred solution of piperidine (28.17 g) in dry ether (100 ml), contained in a flask fitted with reflux condenser. The reaction product was vacuum-distilled from an Arbuzov flask, and after a second distillation a liquid (20 g, 59.5%) was obtained of b.p. 95-96°/3 mm, d_0^{20} 1.0741; n_D^{20} 1.4930; found MR_D 54.95; calculated MR_D 54.77.

Found %: P 15.43; N 6.47

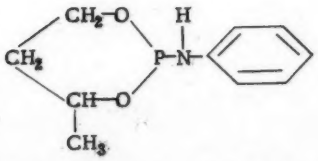
$C_9H_{18}O_2PN$. Calculated %: P 15.26; N 6.89

Action of water on 

Water (0.44 g), slightly acidified with hydrochloric acid, was added dropwise to the ester (5 g). The emulsion formed turned rapidly into a homogeneous solution with rise in temperature to 40°. By vacuum distillation, a substance (2 g) of b.p. 133-134°/4 mm was isolated. By introduction of a few crystals of the previously prepared acid



, it crystallized (m.p. 48-50°). Similar crystals were separated from the residue in the distillation flask.

8. Synthesis of 

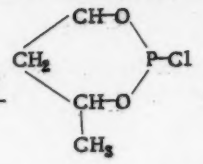
1-Methyltrimethylene phosphorochloridite (21.5 g) was added dropwise to a mixture of aniline (12.94 g), sodium dust (3.2 g), and dry xylene (60 ml). The reaction was accompanied by evolution of heat. When the

whole of the phosphorochloridite had been added, the reaction mixture was heated on the water bath with stirring for one hour. The mixture was cooled, and the colloidal precipitate of sodium chloride and the unchanged sodium were filtered off. The filtrate was distilled twice, giving a product (3 g, 22.8%) of b.p. 136-137°/12 mm; a colorless, very viscous liquid, having a faint but characteristic odor. It was soluble in organic solvents and had d_0^{20} 1.1748; n_D^{20} 1.5558. Found MR_D 57.84; calculated MR_D 57.93.

Found %: P 14.75; N 6.49

$C_{10}H_{14}O_2PN$. Calculated %: P 14.73; N 6.63

It yielded by reaction with CuI a crystalline product having m.p. 134-138° (from benzene-ligroin).

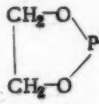
9. Reaction of  with Methylaniline

The reaction was carried out as in the preceding section, the materials taken being: methylaniline (10.7 g), metallic sodium in the form of dust (2.3 g), dry xylene (50 ml), and 1-methyltrimethylene phosphorochloridite (12.64 g). A product (5.1 g, 22.6%) was obtained having b.p. 133-134° at 3 mm; d_0^{20} 1.1382; n_D^{20} 1.5442; found MR_D 62.65; calculated MR_D 62.60.

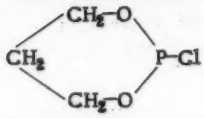
Found %: P 14.03; N 6.42

$C_{11}H_{16}O_2PN$. Calculated %: P 13.77; N 6.22

The product, like the preceding compound, reacts with cuprous chloride and cuprous iodide with rise of temperature. Attempts to isolate the complexes in crystalline form were not successful.

10. Reaction of  with $(C_6H_5)_3CNH_2$

$(C_6H_5)_3CNH_2$ (0.5 g) and ethylene phosphorochloridite (0.25 g) were heated together in dry benzene (5 ml). A precipitate (0.3 g) quickly appeared; the product, after being washed with benzene, melted at 242-246°. The melting point and analytical figures for chlorine (found: Cl 11.19%; calculated Cl 11.99%) corresponded to triphenylmethylamine hydrochloride. It was not found possible to isolate any other product.

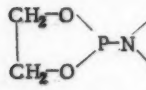
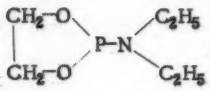
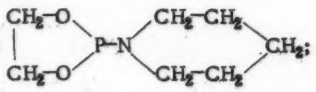
11. Reaction of  with Butylamine

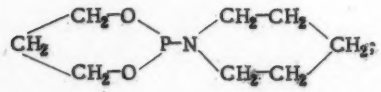
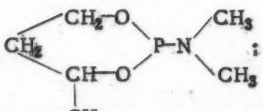
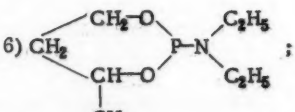
Trimethylene phosphorochloridite, diluted with an equal volume of ether, was added to a solution of butylamine (20 g) in dry ether (180 ml). When the whole of the phosphorochloridite had been added, the mixture was heated on the water bath for 30 minutes. By vacuum fractionation, a substance (3 g) boiling over a wide range of temperature (123-154°/4 mm) with decomposition was separated. A second fractionation was carried out, but again no individual substances were isolated.

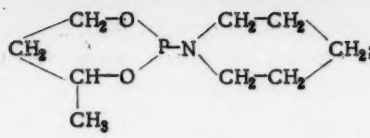
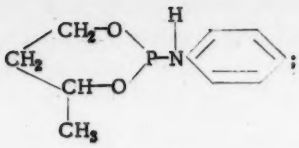
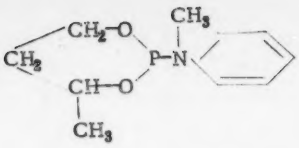
SUMMARY

1. It has been found that cyclic esters of phosphorochloridous acid react with aliphatic and aromatic amines, forming N-substituted cyclic esters of phosphoramidous acid.

2. The following compounds have been synthesized:

1)  ; 2)  ; 3)  ;

4)  ; 5)  ; 6)  ;

7)  ; 8)  ; 9) 

and some of their properties have been studied.

Received June 23, 1952

A. M. Butlerov Chemical Research Institute
of the V. I. Ulyanov-Lenin Kazan State University

LITERATURE CITED

[1] A. E. Arbuzov, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 2, 226 (1946).

[2] A. E. Arbuzov, V. M. Zoroastrova, and N. I. Rizpolozhensky, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 2, 208 (1949); A. E. Arbuzov and M. M. Azanovskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 5, 473 (1949); A. E. Arbuzov and V. M. Zoroastrova, Bull. Acad. Sci. USSR, Div. Chem. Sci., No. 4, 357 (1950); A. E. Arbuzov and V. M. Zoroastrova, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 5, 536 (1951).

PHOSPHOROUS ACID DERIVATIVES CONTAINING A CYCLOHEXYL RADICAL

A. E. Arbuzov and F. G. Valitova

Cyclohexyl derivatives of phosphorous acid have received little study. In 1949 the English chemists Cook, Hett, and others [1] described a method for preparing dicyclohexylphosphorous acid (i.e., dicyclohexyl hydrogen phosphite and/or dicyclohexyl phosphonate), in a yield of 60 - 65% by the action of cyclohexanol on phosphorus trichloride in carbon tetrachloride. No constants other than the boiling point, 135-143°/0.6-1 mm, were cited by the authors. When we attempted to prepare dicyclohexylphosphorous acid by the method of the English chemists, we always obtained a negative result, for at some time during the distillation of the reaction products the contents of the flask always foamed up and then decomposed completely. Repeat experiments invariably resulted in decomposition of the reaction products, and the nature of the conditions necessary for a satisfactory result is not clear*.

Since then we have succeeded in finding a reliable method for preparing dicyclohexylphosphorous acid: by the action of cyclohexanol on phosphorus trichloride (molar ratio 3:1) in presence of pyridine in dry ether. From this reaction two substances were isolated: dicyclohexylphosphorous acid (30% yield) and a small amount of tricyclohexyl phosphite.

Dicyclohexylphosphorous acid is a colorless mobile liquid of characteristic odor having the following constants: b.p. 149-150°/1 mm; d_0^{20} 1.0982; n_D^{20} 1.4800. In ether solution it reacts with metallic sodium forming an ether-soluble salt similar to sodium diethylphosphite. When an ethereal solution of bromotriphenylmethane is added to the ethereal solution of the salt, there appears very rapidly a golden-yellow coloration, characteristic for the triphenylmethyl free radical [2].

By a change in the molecular proportions of cyclohexanol, phosphorus trichloride, and pyridine, it was found possible to go over to the preparation of dicyclohexyl phosphorochloridite. In this case the reaction may be expressed by the equation:

$$2C_6H_{11}OH + PCl_3 + 2C_5H_5N \longrightarrow (C_6H_{11}O)_2PCl + 2C_5H_5N\cdot HCl.$$

When the reaction products are distilled, a readily volatile, somewhat turbid liquid first comes over, and then comes the expected phosphorochloridite. Almost immediately after this has passed over, the contents of the flask foam up and decompose completely. The phosphorochloridite, which is obtained in 40-45% yield, is a colorless, mobile liquid that fumes slightly in air; it has b.p. 152-153°/1 mm; d_0^{20} 1.0811; n_D^{20} 1.4852.

The readily accessible method described above for the preparation of the phosphorochloridite made it possible for us to prepare tricyclohexyl phosphite and a number of other, mixed esters. Starting from the phosphorochloridite we obtained tricyclohexyl phosphite by three methods: 1) by the action of cyclohexanol in presence of pyridine, 2) by the action of cyclohexanol in presence of dimethylaniline, and 3) by the action of the sodium derivative of cyclohexanol (sodium cyclohexyloxide). All the reactions were carried out in a medium of anhydrous ether. The best result was obtained by the action on the phosphorochloridite of sodium cyclohexyloxide, when the yield reached a value of 60-65%.

Tricyclohexyl phosphite, immediately after being distilled, was a colorless viscous liquid of b.p. 175-176° at 1 mm, but after some time the whole of the liquid in the receiver solidified to a mass of clear crystals that tended to stick to one another. When the crystals were removed from the flask and exposed to air, they rapidly became liquid, and to determine their approximate melting point, therefore, a thermometer was inserted into the mass of crystals in the flask: the whole of the contents of the flask was found to melt within the range 60-75°.

By treatment with cuprous bromide, tricyclohexyl phosphite yielded a copper compound that crystallized well from alcohol and melted at 173-174°. We further prepared, by the action of alkoxides on dicyclohexyl

* B. A. Arbuzov (private communication) succeeded on one occasion only in preparing dicyclohexylphosphorous acid in good yield (about 60%) by the method of the English chemists.

phosphorochloridite in a medium of dry ether, a number of mixed esters of formula $(C_6H_{11}O)_2POAlk$, where Alk = CH_3, C_2H_5, C_4H_9, $C_6H_5CH_2$. Boiling points and other constants of the esters obtained are given later in a table.

All the mixed esters obtained were found to react with cuprous bromide with slight evolution of heat (30-40°), forming viscous liquids, which we did not succeed in crystallizing. The "isomerization" reaction carried out on these alkyl dicyclohexyl phosphites proceeded in an extremely peculiar fashion. Thus, when dicyclohexyl methyl phosphite was heated with methyl iodide in a closed tube at 200°, instead of the diminution in the volume of the reaction mixture which is usually observed in these cases, an increase in volume occurred. When the contents of the tube were heated further to 210-220°, the previously homogeneous liquid formed into two layers, the upper and thicker layer being an almost colorless, mobile liquid, and the lower layer being a slightly yellowish, viscous liquid. The tube was opened, and the upper layer was carefully poured off into a small flask and distilled. The greater part of the liquid that came over had a boiling point close to that of cyclohexene; it had the odor of cyclohexene. The tube was cut off almost at the level of the liquid in the lower layer, and the latter was poured off into a small dish, which was placed in a desiccator; the desiccator was evacuated with a water pump. After one day the contents of the dish had crystallized out almost completely. Examination of this substance showed it to be methylphosphonic acid, and here it should be remembered that preparation of methylphosphonic acid in a crystalline form presents a problem that is far from easy. This interesting reaction may be represented by the following equation:

$$(C_6H_{11}O)_2POCH_3 + CH_3I \longrightarrow (C_6H_{11}O)_2P(OCH_3)(CH_3)I \longrightarrow CH_3I + 2C_6H_{10} + CH_3PO(OH)_2.$$

The behavior we have described for dicyclohexyl methyl phosphite is characteristic of that observed in the isomerization reaction carried out on the remainder of the mixed esters (and also tricyclohexyl phosphite) that we have prepared: in all cases there was a small increase in the volume of the reaction mixture when heated to 200°, and then, with rise in temperature to 220°, separation into two layers occurred. The upper layer, independently of the identity of the alkyl radical of the mixed ester, came over mainly in the boiling range of cyclohexene. The lower layer, by analogy with that obtained in the methyl ester experiment, should have contained the corresponding alkylphosphonic acid, but we have not yet succeeded in obtaining the supposed alkylphosphonic acids in a crystalline form. We have not lost hope of doing this in the future by carrying out experiments with greater amounts of starting materials.

In addition to the esters described above, we have prepared yet another mixed ester containing a cyclohexyl group, starting from o-phenylene phosphorochloridite, which we described in a previous communication [3]. By the action of cyclohexanol on o-phenylene phosphorochloridite in presence of pyridine, cyclohexyl-o-phenylene phosphite was obtained in 62% yield. Constants of the ester are given in the table. This ester, unlike the alkyl dicyclohexyl phosphites, gives a well crystallizing copper compound with cuprous bromide (m.p. 137-138°). The crystals of the copper compound are unstable both in air and in a sealed tube: they turn green fairly rapidly, and then turn black. In the isomerization reaction with cyclohexyl iodide or bromide, cyclohexyl o-phenylene phosphite behaves differently from the other mixed esters. When the reactants are heated in a sealed tube to 210°, no appreciable change in volume is to be observed; at temperatures above 210°, decomposition sets in.

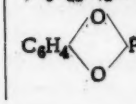
Tricyclohexyl phosphite and cyclohexyl o-phenylene phosphite were taken as examples for the study of the action of bromotriphenylmethane at 180° in sealed tubes. The viscous yellowish masses that were obtained were hydrolyzed by heating with 10% hydrochloric acid in sealed tubes, and in both cases a resinous mass was precipitated, from which, by treatment with alcohol and repeated recrystallization, it was found possible to isolate triphenylmethylphosphonic acid, m.p. 277-278°. By the action of bromotriphenylmethane on dicyclohexyl ethyl phosphite we obtained, unexpectedly, crystals of triphenylmethane, m.p. 92°.

EXPERIMENTAL

Preparation of Dicyclohexylphosphorous Acid $(C_6H_{11}O)_2POH$

An ethereal solution of phosphorus trichloride (22.9 g) was added gradually under stirring to a solution of cyclohexanol (50 g) and pyridine (39.5 g) in dry ether (50 ml). Reaction proceeded with evolution of heat and was continued for three hours. The supernatent ether layer was poured from the precipitate that had formed into a distillation flask. The precipitate was washed with ether by decantation, and the washings were poured into

TABLE 1

No.	Formula	B.p. °C/1 mm	d_0^{20}	n_D^{20}	MR_D found	MR_D calculated	Phosphorus content found	Phosphorus content calculated	Yield %
1	$(C_6H_{11}O)_2POH$	149-150	1.0982	1.4800	63.65	63.57	12.22; 12.37	12.60	39
2	$(C_6H_{11}O)_2PCl$	152-153	1.0811	1.4852	70.11	69.92	11.54; 12.02	11.72	45
3	$(C_6H_{11}O)_3P$	175-176	–	–	–	–	9.30; 9.62	9.45	63
4	$(C_6H_{11}O)_2POCH_3$	127-128	1.0491	1.4750	–	–	12.14; 12.10	11.92	41
5	$(C_6H_{11}O)_2POC_2H_5$	129-130	1.0298	1.4730	75.91	75.52	11.45; 11.57	11.31	33
6	$(C_6H_{11}O)_2POC_4H_9$	139-140	0.9827	1.4618	84.47	84.75	10.52; 10.24	10.26	30.7
7	$(C_6H_{11}O)_2PO-CH_2-C_6H_5$	193-195	1.0594	1.5088	94.65	95.06	9.23; 9.47	9.22	43
8		125-126	1.1661	1.5270	62.76	62.68	12.86; 13.00	13.02	62

the flask. The ether was removed, and the residue was distilled under 1 mm pressure. The following fractions were obtained

Fraction I, b.p. 60-150°; 5 g; n_D^{20} 1.4802

Fraction II, b.p. 150-160°; 19 g; d_0^{20} 1.4812

Fraction III, b.p. 166-179°; 5 g - crystallized out

Fractions II and III were redistilled, yielding a fraction (16 g, 39%) of b.p. 149-150°; n_D^{20} 1.4800; d_0^{20} 1.0982; found MR_D 63.65; calculated MR_D 63.57.

Found %: P 12.22, 12.37

$C_{12}H_{23}O_3P$. Calculated %: P 12.60

Preparation of Dicyclohexyl phosphorochloridite $(C_6H_{11}O)_2PCl$

An ethereal solution of phosphorus trichloride (69 g) was added under stirring to a solution of cyclohexanol (100 g) and pyridine (79 g) in ether. Reaction proceeded with evolution of heat, and it continued for four hours. On the next day the supernatent ether layer was poured off into a distillation flask, and ether washings decanted from the precipitate were added. The ether was removed, and the residue was distilled under a pressure of 1 mm. Two fractions were obtained: a turbid fraction, b.p. 152-153°, and a clear fraction, b.p. 140-160°; heating at above 160° led to decomposition. After two distillations a fraction (61 g, 45%) was obtained having b.p. 152-153°, n_D^{20} 1.4852; d_0^{20} 1.0811; found MR_D 70.11; calculated MR_D 69.92.

Found %: P 11.54; 12.02

$C_{12}H_{22}O_2P$. Calculated %: P 11.72

Found %: Cl 13.85; 13.62

$C_{12}H_{22}O_2PCl$. Calculated %: Cl 13.42;

Preparation of Tricyclohexyl Phosphite $(C_6H_{11}O)_3P$

1. In presence of pyridine. An ethereal solution of dicyclohexyl phosphorochloridite (31 g) was added slowly under stirring to an ethereal solution of cyclohexanol (11.7 g) and pyridine (9.2 g). When reaction was complete, the crystalline precipitate was rapidly filtered off and washed with dry ether. The filtrate was distilled to remove ether, and the residue was fractionated under a pressure of 1 mm. The following fractions were obtained:

Fraction I, b.p. 65-158°; 4.5 g

Fraction II, b.p. 158-168°; 11.5 g

Fraction III, b.p. 168-180°; 15.6 g

Further distillation of Fractions II and III yielded a fraction of b.p. 175-176°, which crystallized in the receiver (16 g, 41%).

Found %: P 9.30; 9.62

$C_{18}H_{33}O_3P$. Calculated %: P 9.45

2. In presence of dimethylaniline. An ethereal solution of the phosphorochloridite (10 g) was added to an ethereal solution of cyclohexanol (3.8 g) and dimethylaniline (4.5 g). The supernatent ethereal layer was poured off into a distilling flask, and the ether was distilled off. The residue was distilled under a pressure of 1 mm Hg, and the following fractions were isolated:

Fraction I, b.p. 50-150°; 1.3 g

Fraction II, b.p. 150-160°; 4.2 g

Fraction III, b.p. 160-180°; 5.5 g

A second distillation of Fraction III yielded a fraction (4 g, 32%), of b.p. 175-176°, which crystallized.

Action of the phosphorochloridite on sodium cyclohexyloxide. An ethereal solution of the phosphorochloridite (10 g) was added to an ethereal solution of sodium cyclohexyloxide prepared from metallic sodium (0.87 g) and cyclohexanol (3.8 g) by the "swelling" technique [4]. The precipitate present was filtered off, and the filtrate was distilled. The thick oil that remained after removal of ether distilled over at 175-176° and completely solidified. In this case there were no other fractions. The melting point of the crystals was determined with a thermometer placed in the flask. The substance melted completely in the range 60-75°. The yield of the ester was 7.8 g (63%).

Action of cuprous bromide on tricyclohexyl phosphite. Tricyclohexyl phosphite (1 g) and cuprous bromide (0.43 g) were introduced into a small flask. A thermometer placed in the mixture indicated a rise in temperature to 42°, after which no further rise occurred. The white mass formed was recrystallized twice from dry alcohol; it melted at 173-174°.

Found %: Br 9.75; 9.55

$C_{36}H_{66}O_6P_2CuBr$. Calculated %: Br 9.99

Preparation of Alkyl Dicyclohexyl Phosphites

Alkyl dicyclohexyl phosphites were prepared by the action in a dry ether medium of dicyclohexyl phosphorochloridite on sodium alkoxides. When reaction was complete, the ethereal solution was either filtered off from the precipitate that had formed, or separated by submitting the contents of the flask to centrifuging. The filtrate was fractionated (under reduced pressure when the ether had been removed).

1. Preparation of dicyclohexyl methyl phosphite. The materials taken for reaction were: the phosphorochloridite (13 g), methanol (1.6 g), and sodium (1.15 g). After removal of ether the residue was distilled at 1 mm, and the following fractions were obtained:

Fraction I, b.p. 60-120°

Fraction II, b.p. 120-140°

After two distillations a fraction (5.3 g, 41%) of b.p. 127-128° was obtained; it had n_D^{20} 1.4750; d_0^{20} 1.0491.

Found %: P 12.14; 12.10

$C_{13}H_{25}O_3P$. Calculated %: P 11.92

2. Preparation of dicyclohexyl ethyl phosphite. The phosphorochloridite (10 g) was added to sodium ethoxide prepared from sodium (0.85 g) and ethanol (1.7 g). Fractionation of the reaction products yielded the fractions:

Fraction I, b.p. 80-120°

Fraction II, b.p. 120-135°

After a second distillation a fraction of b.p. 129-130°/1 mm (3.4 g, 33%) was isolated. It had n_D^{20} 1.4730; d_0^{20} 1.0298; found MR_D 75.91; calculated MR_D 75.52.

Found %: P. 11.45; 11.57

$C_{14}H_{27}O_3P$. Calculated %: P 11.31

3. Preparation of butyl dicyclohexyl phosphite. An ethereal solution of the phosphorochloridite (10 g) was added to sodium butoxide prepared from sodium (0.81 g) and butyl alcohol (2.04 g). After distillation of the products of the reaction the following fractions were obtained:

Fraction I, b.p. 80-130°
Fraction II, b.p. 130-150°

After a second distillation a fraction (3.5 g, 30.7%) was obtained of b.p. 139-140°/1 mm and having n_D^{20} 1.4618; d_0^{20} 0.9827; found MR_D 84.47; calculated MR_D 84.75.

Found %: P 10.52; 10.24
$C_{16}H_{31}O_3P$. Calculated %: P 10.26

4. Preparation of benzyl dicyclohexyl phosphite. Sodium benzyloxide was prepared in this case not by the swelling technique, but by the action of benzyl alcohol (16 g) on sodium (3.45 g) in dry ether, heat being applied. To the solution obtained an ethereal solution of the phosphorochloridite (40 g) was added. When reaction was complete, the ether layer was distilled (under reduced pressure when the ether had been removed). The following fractions were obtained:

Fraction I, b.p. 80-160°
Fraction II, b.p. 160-200°

After a second distillation a fraction (22 g, 43%) of b.p. 193-195° was obtained; it had n_D^{20} 1.5088; d_0^{20} 1.0594; found MR_D 94.65; calculated MR_D 95.06.

Found %: P 9.23; 9.37
$C_{19}H_{29}O_3P$. Calculated %: P 9.22

5. Preparation of cyclohexyl o-phenylene phosphite. An ethereal solution of o-phenylene phosphorochloridite (20 g) was added under stirring to an ethereal solution of cyclohexanol (11.5 g) and pyridine (9.8 g). Reaction set in, heat being evolved. The supernatent ethereal layer was distilled, the oil that remained after removal of ether being distilled under 1 mm pressure. The following fractions were obtained:

Fraction I, b.p. 80-120°, 3 g
Fraction II, b.p. 120-130°; 18 g

A second distillation yielded a fraction (17 g, 62%) of b.p. 125-126°; it had n_D^{20} 1.5270; d_0^{20} 1.1661; found MR_D 62.76; calculated MR_D 62.68.

Found %: P 12.86; 13.00
$C_{12}H_{15}O_3P$. Calculated %: P 13.02

Action of cuprous bromide on cyclohexyl o-phenylene phosphite. Cuprous bromide (1.8 g) was introduced into a flask containing cyclohexyl o-phenylene phosphite (2 g). The temperature of the mixture rose to 45°. The white mass obtained was recrystallized twice from absolute alcohol, yielding crystals of m.p. 137-138°. Further recrystallization did not affect the melting point. After a day's exposure to the atmosphere the crystals turned green; they then began to blacken.

Found %: P 8.72; 8.49
$C_{12}H_5O_3PCuBr$. Calculated %: P 8.12

Attempted isomerization of dicyclohexyl methyl phosphite in presence of methyl iodide. A mixture of dicyclohexyl methyl phosphite (2.5 g) and methyl iodide (1.4 g) was heated in a sealed tube having a constriction for facilitating observation of volume change. On being heated to 200°, the liquid increased in volume. Between 200° and 215° two layers formed. The upper layer was carefully poured off into a small flask and was distilled under normal pressure. Two fractions were obtained: one of b.p. 40-80°, the boiling temperature of which rose rapidly (about one-third of the total); and one of b.p. 80-85° having an odor similar to that of cyclohexene.

The lower layer was poured onto a watch glass and left in a desiccator; it had solidified by the next day. The unpurified crystals melted at 98-100° (melting point of methylphosphonic acid, 103-104°).

Action of bromotriphenylmethane on cyclohexyl o-phenylene phosphite. A mixture of the ester (2 g) and bromotriphenylmethane (2.7 g) was heated in a sealed tube to 180°. A thick yellow liquid was formed. The

contents of the tube were submitted to a hydrolysis treatment, 15% hydrochloric acid (10 ml) being added in the tube, which was heated at 200° for four hours. A resin came down, and the formation of crystals was noted in the aqueous layer. The resin was first purified by crystallization from benzene, and the resulting gray crystals were recrystallized from dry alcohol. The crystals obtained melted at 277-278°, the melting point of triphenylmethylphosphonic acid.

Action of bromotriphenylmethane on tricyclohexyl phosphite. A mixture of tricyclohexyl phosphite (2 g) and bromotriphenylmethane (2 g) was heated in a sealed tube at 180° for one hour. The contents of the tube consisted of a thick, slightly colored liquid, at the bottom of which a resin had formed. After an addition of 15% hydrochloric acid (10 ml), the tube was again heated at 190° for two hours. When the tube had cooled, hairlike crystals of triphenylmethylphosphonic acid were precipitated in the aqueous layer. The crystals melted, after purification, at 277-278°.

SUMMARY

1. Reliable methods for the preparation of dicyclohexylphosphorous acid, of dicyclohexyl phosphorochloridite, and of tricyclohexyl phosphite have been found.

2. The following mixed esters of phosphorous acid have been prepared: methyl, ethyl, butyl, and benzyl dicyclohexyl; and cyclohexyl o-phenylene.

3. Methyl, ethyl, butyl, and benzyl dicyclohexyl phosphites react with cuprous halides, forming viscous liquids that do not crystallize.

4. Tricyclohexyl phosphite and cyclohexyl o-phenylene phosphite form well crystallizing complex compounds with cuprous bromide.

5. Methyl, ethyl, butyl, and benzyl dicyclohexyl phosphites behave in a peculiar fashion in the isomerization reaction with the corresponding alkyl halides at 200-220°, cyclohexane and the corresponding alkylphosphonic acids being formed.

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LITERATURE CITED

[1] H. G. Cook, J. D. Hett et al. J. Chem. Soc. 2921 (1949).

[2] A. E. Arbuzov and B. A. Arbuzov, J. Russ. Phys. Chem. Soc. 61, 1923 (1929).

[3] A. E. Arbuzov and F. G. Valitova, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 4, 533 (1940).

[4] A. E. Arbuzov, "Catalysis Phenomena Associated with the Reactions of certain Phosphorus Compounds", A monograph, p. 144 (1914).

COMPLEX COMPOUNDS OF PHOSPHOROUS ESTERS

COMMUNICATION 1. COMPOUNDS WITH COPPER, SILVER, AND GOLD SALTS

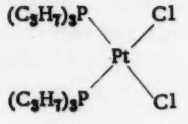
A. E. Arbuzov and V. M. Zoroastrova

The complex compounds of phosphines and arsines with metal salts have been studied in some detail, and their investigation is being pursued with vigor at the present time. The complex compounds formed with tertiary phosphines comprise the following principal types [1]:

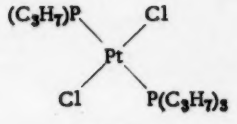
Bromides and iodides of univalent copper and silver unite with phosphines, giving a type of complex (I and II) having a quadruple molecular weight: $[R_3P{\cdot}CuI]_4$ (I), and $[R_3P{\cdot}AgI]_4$ (II).

Halides of univalent gold give simple linear molecules of the type: $R_3P \longrightarrow AuCl$ (III).

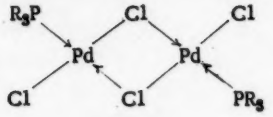
Salts of bivalent metals, e.g., palladous chloride or platinous chloride, give complex compounds of the following types: those formed from one molecule of salt, $(R_3P)_2PdCl_2$ (IV), having a planar configuration and being able to exist in cis and trans forms (V and VI), and bridged forms (VII), having a planar molecule of trans configuration:



(V) (cis)



(VI) (trans)



(VII)

The halides of mercury and cadmium give compounds conforming to types IV and VII in constitution, but having a tetrahedral arrangement about the central atom. Mercury and cadmium salts may give also compounds of the types $[(R_3P)_2 (HgBr_2)_3]$ and $[(R_3P)_2 (HgBr_2)_4]$.

The complex compounds of phosphorous esters have been studied to a considerably less extent. Schutzenberger [2] by the action of alcohols on $PtCl_2{\cdot}PCl_3$ and $PtCl_2{\cdot}2PCl_3$ obtained $PtCl_2{\cdot}P(OCH_3)_3$, and $PtCl_2{\cdot}2P(OCH_3)_3$, $PtCl_2{\cdot}P(OC_2H_5)_3$ and $PtCl_2{\cdot}2P(OC_2H_5)_3$. Pomey [3] prepared $PtCl_2{\cdot}P(OC_3H_7)_3$, and Risler [4] prepared $PtCl_2{\cdot}P(OC_5H_{11})_3$ by similar methods. Lindet [5] by the action of methanol and of ethanol on $AuCl{\cdot}PCl_3$, obtained $AuCl{\cdot}P(OCH_3)_3$ and $AuCl{\cdot}P(OC_2H_5)_3$.

One of us [6] has shown that full esters of phosphorous acid give complex compounds with cuprous halides of the types $CuX{\cdot}P(OR)_3$ and $CuX{\cdot}2P(OR)_3$. Full esters of phosphorous acid react also with silver halides giving complex compounds of the type $AgX{\cdot}P(OR)_3$ [7].

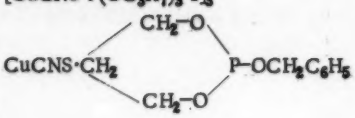
Grinberg and Troitskaya [8] prepared a number of complex platinum compounds, using trialkyl phosphites and dialkylphosphorous acids as addends, and studied their properties. In this work a strong analogy was revealed between phosphonic and phosphorous derivatives. Recently, we have undertaken a more detailed study of the previously prepared complex compounds of full phosphorous esters, and we have prepared new complex derivatives of trialkyl phosphites.

In the present communication we give the results on copper, silver and gold compounds. As already indicated, full phosphorous esters give complexes of the types $CuX{\cdot}P(OR)_3$ and $CuX{\cdot}2P(OR)_3$, with cuprous halides.

Molecular weights have already been determined for some of the compounds of the first type [6]. Ebullioscopic measurements in chloroform on $CuCl \cdot P(OCH_3)_3$ and $CuBr \cdot P(OCH_3)_3$ gave for the first compound M = 374 instead of 223.5, or for the double molecule 447, and for the second compound 576 instead of 268, or for the double molecule 536. Cryoscopic measurements in benzene on $CuI \cdot P(OC_2H_5)_3$ gave M = 1088, corresponding to a triple molecular weight (1071). Thus the results obtained do not give a clear idea of the molecular weights of these complex compounds.

Since partial decomposition of the complex may occur in the course of molecular-weight determination in boiling chloroform, we have measured the molecular weights cryoscopically in benzene and have obtained the results given in Table 1.

TABLE 1

No.	Formula	B.p. °C	Molecular weight	
			found	calculated
1	$[CuCl \cdot P(OC_3H_7)_3\text{-}i]_3$	112-114	921.6	921.57
2	$[CuBr \cdot P(OC_3H_7)_3\text{-}i]_3$	149-150	1059.8	1054.9
3	$[CuI \cdot P(OC_3H_7)_3\text{-}i]_3$	184-185	1192.6	1195.98
4	$[CuCl \cdot P(OC_6H_5)_3]_3$	95- 96	1220.1	1227.5
5	$[CuBr \cdot P(OC_6H_5)_3]_3$	90.5-91.5	1363.8 1342.4	1360.8
6	$[CuCNS \cdot P(OC_3H_7)_3\text{-}i]_3$	95-96	1047.8	989.4
7		150-152 (dec.)		

Results are given in Table 1 for the new complex compound of triisopropyl phosphite with copper thiocyanate which we have prepared. The molecular-weight results show that complexes of the type $CuX \cdot P(OR)_3$ have triple molecules and differ, therefore, from the analogous complexes with phosphines ($CuX \cdot PR_3$), to which quadrupled molecular weights are ascribed [9]. It should be noted, however, that the experimental values for the molecular weights of $CuX \cdot PR_3$ lie between the triple and quadruple values.

Molecular weights have hitherto not been determined for compounds of the type $CuX \cdot 2P(OR)_3$. We have determined the molecular weights cryoscopically in benzene and have thus shown that the compounds $CuX \cdot 2P(OR)_3$ are in the form of simple molecules (Table 2).

TABLE 2

No.	Formula	B.p. °C	Molecular weight	
			found	calculated
1	$CuCl \cdot 2P(OC_6H_5)_3$	70	606.3	719.2
2	$CuBr \cdot 2P(OC_6H_5)_3$	73-74	697.4	763.7
3	$CuI \cdot 2P(OC_6H_5)_3$	73-76	713.1	810.7

We have found no data in the literature concerning compounds of the type $CuX \cdot 2PR_3$. Nyholm [10] has recently described the complexes $CuX \cdot 2AsR_3$. Cryoscopic measurements of molecular weight in benzene and nitrobenzene gave figures lying between the single and double values. Nyholm considers the double value to be the more probable, the observed lowering of the value being probably to be explained by dissociation of the complex in solution; but he considers that the question of the molecular weight of $CuX \cdot 2AsR_3$ remains open.

It is interesting to note that cryoscopic measurements in benzene and in nitrobenzene of the molecular weights of the complexes $CuX \cdot AsR_3$ give, according to Nyholm, values that correspond to triple molecules, although Nyholm assumes quadruple values for them.*

A. E. Arbuzov and Kartashev [7] have obtained by the action of triethyl phosphite on silver salts the complexes $(C_2H_5O)_3P \cdot AgX$, where X = Cl, Br and I. These complexes were not investigated more closely.

We have obtained hitherto undescribed complexes of AgX with isopropyl phosphite and have determined their molecular weights cryoscopically in benzene. The results are given in Table 3.

* For $CuCl \cdot AsR_3$ the calculated molecular weight is 343, and the values found are 1205 (nitrobenzene) and 1020 (benzene); the calculated values for trimer and tetramer are 1029 and 1372 respectively. For $CuBr \cdot AsR_3$ the calculated molecular weight is 387.5, and the value found in benzene is 1260; the calculated value for trimer is 1162.5.

TABLE 3

No.	Formula	B.p. °C	Molecular weight	
			found	calculated
1	$[AgCl{\cdot}P(OC_3H_7\text{-}i)_3]_3$	29-30	814.4 1233.3	1054
2	$[AgBr{\cdot}P(OC_3H_7\text{-}i)_3]_3$	73-75	1216.5	1187.9
3	$[AgI{\cdot}P(OC_3H_7\text{-}i)_3]_3$	163-164	1326.9	1328.9

As will be seen from Table 3, the complexes of triisopropyl phosphite with AgX (X = Cl, Br and I) have triple molecules in benzene solution and are therefore analogous to the complexes $CuX{\cdot}P(OR)_3$. It should be noted that the complexes $CuX{\cdot}PR_3$ and $AgX{\cdot}PR_3$ have the same type of structure and have association factors in benzene solution of between 3.5 and 4. We have not succeeded in preparing compounds between triphenyl phosphite and silver halide.

As already stated, Lindet [5] by the action of methanol and of ethanol on the complex $AuCl{\cdot}PCl_3$ has obtained the complexes $AuCl{\cdot}P(OCH_3)_3$ and $AuCl{\cdot}P(OC_2H_5)_3$. We have prepared the complex with trimethyl phosphite by three different methods: a) by Lindet's method, by the action of trimethyl phosphite on $AuCl{\cdot}PCl_3$, b) by the action of trimethyl phosphite on AuCl, and c) by the action of trimethyl phosphite on $AuCl{\cdot}PCl_3$. In all cases the same compound of m.p. 101-102° was obtained. Also, we have obtained by the action of triphenyl phosphite on $AuCl{\cdot}PCl_3$ the previously undescribed complex $(C_6H_5O)_3P{\cdot}AuCl$, m.p. 103°, and we have prepared a liquid complex of AuCl with triisopropyl phosphite.

Molecular-weight determinations by cryoscopy in benzene of the crystalline complexes obtained gave results corresponding to single molecules (Table 4).

TABLE 4

No.	Formula	B.p. °C	Molecular weight	
			found	calculated
1	$(CH_3O)_3P{\cdot}AuCl$	101-102	348	356.7
2	$(C_6H_5O)_3P{\cdot}AuCl$	103	514.4	542.5

Thus, the complexes formed between phosphorous esters and gold (I) chloride have structures analogous to those of the complexes between gold (I) chloride and phosphines.

EXPERIMENTAL

Molecular Weight Determinations by the Cryoscopic Method on Complex Compounds formed between Triisopropyl Phosphite and Cuprous Halides

Compounds 1, 2 and 3 were prepared first by A. E. Arbuzov in 1905.

1) $P(OC_3H_7)_3{\cdot}CuCl$, m.p. 112-114° (from petroleum ether)
2) $P(OC_3H_7)_3{\cdot}CuBr$, m.p. 149-150° (from petroleum ether)
3) $P(OC_3H_7)_3{\cdot}CuI$, m.p. 184-185° (from ether)

Compound 1:

Found: M 921.6
Calculated for $[P(OC_3H_7\text{-}i)_3{\cdot}CuCl]$: M 307.19
" $[P(OC_3H_7\text{-}i)_3{\cdot}CuCl]_3$: M 921.57

Compound 2:

Found: M 1059.8
Calculated for $[P(OC_3H_7\text{-}i)_3{\cdot}CuBr]$: M 351.64
" $[P(OC_3H_7\text{-}i)_3{\cdot}CuBr]_3$: M 1054.95

Compound 3:

Found: M 1192.6
Calculated for $[P(OC_3H_7\text{-}i)_3{\cdot}CuI]$: M 398.65
" $[P(OC_3H_7\text{-}i)_3{\cdot}CuI]_3$: M 1195.95

Determination of the Molecular Weights of Complex Compounds formed between Triphenyl Phosphite and Cuprous Halides

Five compounds formed between triphenyl phosphite and cuprous halides are known (they were first prepared by A. E. Arbuzov):

1) $CuCl \cdot P(OC_6H_5)_3$, m.p. 95-96°
2) $CuBr \cdot P(OC_6H_5)_3$, m.p. 90.5-91.5°
3) $CuCl \cdot 2P(OC_6H_5)_3$, m.p. 70°
4) $CuBr \cdot 2P(OC_6H_5)_3$, m.p. 73-74°
5) $CuI \cdot 2P(OC_6H_5)_3$, m.p. 73-76°

The molecular weights were determined cryoscopically in benzene:

Compound 1:

Found: M 1220.1
Calculated for $[CuCl \cdot P(OC_6H_5)_3]$: M 409.15
" $[CuCl \cdot P(OC_6H_5)_3]_3$: M 1227.45

Compound 2:

Found: M 1363.8; 1342.4
Calculated for $[CuBr \cdot P(OC_6H_5)_3]$: M 453.61
" $[CuBr \cdot P(OC_6H_5)_3]_3$: M 1360.83

Compound 3:

Found: M 606.3
Calculated for $CuCl \cdot 2P(OC_6H_5)_3$: M 719.24

Compound 4:

Found: M 697.4
Calculated for $CuBr \cdot 2P(OC_6H_5)_3$: M 763.72

Compound 5:

Found: M 713.1
Calculated for $CuI \cdot 2P(OC_6H_5)_3$: M 810.7

Preparation of Complex Compounds between Phosphorous Esters and Salts of Silver, Copper, and Gold

1. Preparation of $P(OC_3H_7\text{-}i)_3AgCl$. Silver chloride (0.73 g) was added to triisopropyl phosphite (1.2 g). The temperature of the reaction mixture rose to 40°, but in order to dissolve the residual salt the mixture was cautiously heated over a burner at 50-55°. When reaction was complete, the product was dissolved in absolute alcohol; the small amount of precipitate present was filtered off, and the solution was poured into snow-cooled water. The oil that separated crystallized when rubbed out with a glass rod. The crystals obtained melted at 28-30°. After being recrystallized from ether, the product melted at 29-30°.

Found %: Cl 9.83
$C_9H_{21}O_3PAgCl$. Calculated %: Cl 10.08

Determination of the molecular weight cryoscopically in benzene gave the following result:

Found: M 814.4
Calculated for $[P(OC_3H_7\text{-}i)_3 \cdot AgCl]$: M 351.5
" $[P(OC_3H_7\text{-}i)_3 \cdot AgCl]_3$: M 1054

2. Preparation of $P(OC_3H_7\text{-}i)_3 \cdot AgBr$. Silver bromide (1.7 g) was added in portions to triisopropyl phosphite (1.8 g, i.e., one mole per mole of the salt). As in the first experiment, the mixture became warm with the reaction. When the temperature fell, the mixture was heated to 50° and dissolved in absolute alcohol; it was then filtered and poured into cold water. The oil that formed solidified rapidly. The crystalline product was filtered off, dried on filter paper, and recrystallized from dry ether, giving colorless crystals (2.3 g), m.p. 73-75°, soluble in many organic solvents, but insoluble in water; in presence of water and in the light they darkened with separation of silver.

Found %: Br 20.39
$C_9H_{21}O_3PAgBr$. Calculated %: Br 20.18

Found: M 1233.3; 1216.5 (cryoscopic)
Calculated for $[P(OC_3H_7\text{-}i)_3 \cdot AgBr]$: M 395.95
" $[P(OC_3H_7\text{-}i)_3 \cdot AgBr]_3$: M 1187.85

3. Preparation of $P(OC_3H_7\text{-}i)_3 \cdot AgI$. The complex compound of triisopropyl phosphite with silver iodide was obtained by a method similar to that just described from 1 g of the ester and 1.17 g of the salt. To complete the reaction, the mixture was carefully heated at 50-55° over a bunsen flame. When the test tube was cooled, the product rapidly solidified. Two crystallizations from ether and one from absolute alcohol yielded well formed colorless crystals of m.p. 163-164° (dec). The reaction product was similar to the previous products in properties: soluble in ether, benzene, acetone, methanol, and ethanol; insoluble in water; yellows on standing.

	Found %:	I 28.83
$C_9H_{21}O_3PAgI$.	Calculated %:	I 28.65

	Found:	M 1326.9 (cryoscopic)
Calculated for	$[P(OC_3H_7\text{-}i)_3 \cdot AgI]$:	M 442.97
"	$[P(OC_3H_7\text{-}i)_3 \cdot AgI]_3$:	M 1328.91

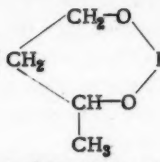
4. Action of silver halides on triphenyl phosphite. Silver iodide (1.2 g) was added to triphenyl phosphite (1.5 g). Reaction did not set in: the temperature remained unchanged, and the salt did not dissolve in the ester. The mixture was heated, at first at 55°, later at a higher temperature (about 100°), and finally at 150-155°. Part of the silver iodide then dissolved. After treatment of the reaction mixture with absolute alcohol and with water, an oil was obtained which did not crystallize after strong cooling and long standing. Attempts to prepare complex compounds of triphenyl phosphite with silver bromide and with silver chloride also did not give positive results.

5. Preparation of the complex compound of triisopropyl phosphite with cuprous thiocyanate. Cuprous thiocyanate (1.4 g) was added to triisopropyl phosphite (2.2 g). Reaction set in, and the temperature of the mixture rose to 60°. The white greasy material that formed solidified on standing. After several recrystallizations from absolute ether, a product was obtained that melted with decomposition at 95-96°. It was of good solubility in ether, benzene, acetone, ligroin, methanol, and ethanol. From its solutions, a precipitate of cuprous thiocyanate separated on standing.

	Found %:	P 9.64; 9.81; S 9.88
$C_{10}H_{21}O_3PCuNS$.	Calculated %:	P 9.40 S 9.72

	Found:	M 1047.8 (cryoscopic)
Calculated for	$[P(OC_3H_7\text{-}i)_3 \cdot CuCNS]$:	M 329.8
"	$[P(OC_3H_7\text{-}i)_3 \cdot CuCNS]_2$:	M 659.5
"	$[P(OC_3H_7\text{-}i)_3 \cdot CuCNS]_3$:	M 989.4

6. Preparation of the complex compound of triphenyl phosphite with cuprous thiocyanate. Cuprous thiocyanate (0.8 g) was added to triphenyl phosphite (2 g, i.e., one mole per mole of the thiocyanate). A very slow reaction with insignificant rise in temperature set in (in 7-10 minutes the temperature rose from 20° to 26°). The mixture was heated at 85-90° on the water bath for several minutes. On cooling, a solid gray mass was formed which was readily soluble in ether, benzene, and other solvents, but insoluble in water. When practically the whole of the solvent had been evaporated off, there remained a white solid having a wide melting range (50-56°). The product melted to a milky liquid, which did not resolidify on cooling. It was not found possible to obtain a product having a sharp melting point.

7. Preparation of 

Cuprous thiocyanate (0.46 g) was added to benzyl 1-methyltrimethylene phosphite (0.8 g, i.e., one mole per mole of CuCNS). The temperature of the mixture rose to 50°, and a thick white mass was formed. To complete the reaction, the mixture was heated for ten minutes in a glycerol bath at 80°. It was then treated with benzene. After evaporation of the benzene, a solid remained in the dish; it was soluble in ether, alcohol, acetone, and dioxane, but was insoluble in water. It melted at 150-152° (it began to sinter together somewhat below this temperature). Its alcoholic solution rapidly became turbid owing to separation of CuCNS.

	Found %:	P 8.40; S 10.28
$C_{12}H_{15}O_2PCuCNS$.	Calculated %:	P 8.91; S 9.21

8. Preparation of the complex compound of trimethyl phosphite with aurous chloride. Expt. 1. Action of methanol on the complex $AuCl \cdot PCl_3$. The inorganic complex of aurous chloride with phosphorus trichloride was prepared by heating aurous chloride with excess of phosphorus trichloride for two hours under reflux (Schutzenberger's method). In the flask, after removal of excess of phosphorus trichloride, there remained long needles of the complex, which are extremely unstable to atmospheric moisture. A small amount of the $AuCl \cdot PCl_3$ complex was dissolved in excess of absolute methanol. Reaction proceeded with inappreciable evolution of heat. On evaporation of the methanol, grayish crystals came down, and these, after recrystallization from methanol, were obtained as colorless needles, m.p. 101-102°. When heated above the melting point, the product darkened and metallic gold separated out.

Expt. 2. Action of trimethyl phosphite on the complex $AuCl \cdot PCl_3$. Trimethyl phosphite (0.17 g) was added to $AuCl \cdot PCl_3$ (0.5 g, i.e., one mole per mole of phosphite) and was dissolved in dry benzene (4 ml). The excess of benzene and phosphorus trichloride was removed under reduced pressure. On standing, crystals came down which, after being washed with ether, melted at 95-101°. The product was purified by recrystallization from methanol, giving needles, m.p. 101°, which melted, in admixture with the product obtained in Expt. 1, at 101-102°.

Expt. 3. Action of AuCl on trimethyl phosphite. Trimethyl phosphite (0.28 g) was dissolved in dry ether (5 ml). An equimolecular proportion of aurous chloride was added to the solution in small amounts at a time, and the substances reacted with evolution of much heat and with separation of a small amount of colloidal gold. After evaporation of the ether, crystals of m.p. 101° were obtained in insignificant yield. It was undepressed in melting point when mixed with the product of Expt. 1. It was of good solubility in ether, benzene, and alcohol, but insoluble in water. The molecular weight was determined cryoscopically in benzene:

Found: M 348
$C_3H_9O_3PAuCl$. Calculated: M 356.73

9. Preparation of the complex compound of triisopropyl phosphite with aurous chloride. Expt. 1. Action of isopropyl alcohol on the complex $AuCl \cdot PCl_3$. A small amount of the complex $AuCl \cdot PCl_3$ was treated with anhydrous isopropyl alcohol. The mixture grew warm. When the excess of isopropyl alcohol had been removed under reduced pressure, a liquid product, which could not be caused to crystallize, remained in the flask.

Expt. 2. Action of AuCl on triisopropyl phosphite. a) Aurous chloride (0.16 g) was added in two portions to triisopropyl phosphite (0.28 g, i.e. one mole per mole of AuCl). With each addition of the salt, the temperature of the mixture rose to 43-45°. The reaction product was treated with dry ether, and the solution was filtered from the small residue of AuCl and was set aside for crystallization. However, when the ether had evaporated, the product did not crystallize. Snow cooling did not induce crystallization.

b) The experiment was carried out in ether solution, triisopropyl phosphite (0.34 g) dissolved in dry ether being treated with an equimolecular proportion of aurous chloride. Reaction occurred with evolution of heat and hissing (boiling of the ether at the point at which the reagents came into contact). The liquid first became yellow, and then became colorless again. It was filtered, and the clear liquid was left in a desiccator over sulfuric acid. After the liquid had stood overnight, the walls of the flask were covered with a gold mirror.

10. Preparation of the complex compound of triphenyl phosphite with aurous chloride. Triphenyl phosphite was added dropwise to $AuCl \cdot PCl_3$ (1.2 g) in benzene solution. Reaction occurred, and the mixture grew warm. When a part of the benzene had been evaporated, large glistening crystals (0.8 g, prisms) came down. The product, after recrystallization from ether, melted at 103° (when it was heated further, metallic gold separated). It was soluble in ether, benzene, acetone, and other solvents, but insoluble in water. After being stored for a long time, it became dirty pink in color.

Found %: Au 35.81; P 5.74
$C_{18}H_{15}O_3PAuCl$. Calculated %: Au 36.33; P 5.71

Found: M 514.43 (cryoscopic)
$C_{18}H_{15}O_2PAuCl$. Calculated: M 542.48

SUMMARY

1. The synthesis has been performed for the first time of complex compounds of triisopropyl phosphite with silver halides and of complex compounds of triisopropyl phosphite and of benzyl 1-methyltrimethylene phosphite with cuprous thiocyanate.

2. The molecular weights have been determined by the cryoscopic method of complex compounds of certain full esters of phosphorous acid with copper and silver halides. For compounds of the type $P(OR)_3 \cdot AgX$, $P(OR)_3 \cdot CuX$, $P(OR)_3 \cdot CuCNS$, values corresponding to triple molecules have been obtained.

3. Complex compounds of triisopropyl phosphite and of triphenyl phosphite with aurous chloride have been synthesized. Determination of their molecular weights by the cryoscopic method (benzene solution) has shown that they occur in the monomeric form.

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LITERATURE CITED

[1] J. Allison and F. Mann, J. Chem. Soc. 2915 (1949).

[2] P. Schutzenberger, Bull. Soc. chim. 17, 482 (1872); 18, 101 (1872).

[3] E. M. Pomey, Jahresber. 612 (1887).

[4] M. Risler, Bull. Soc. chim. 18, 151 (1872).

[5] M. L. Lindet, Ann. Chim. (6) 11, 190 (1887).

[6] A. E. Arbuzov, "The Structure of Phosphorous Acid and its Derivatives", St. Petersburg, 1905, p. 32.

[7] A. E. Arbuzov and A. V. Kartashev, J. Russ. Phys. Chem. Soc. 45, 79 (1913).

[8] A. A. Grinberg and A. D. Troitskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 4, 178 (1944); A. A. Grinberg, Z. A. Razumova, and A. D. Troitskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 3, 253 (1946).

[9] F. Mann, D. Purdie and A. Wells, J. Chem. Soc. 1506 (1936).

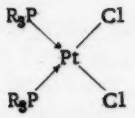
[10] R. S. Nyholm, J. Chem. Soc. 1257 (1952).

COMPLEX COMPOUNDS OF PHOSPHOROUS ESTERS

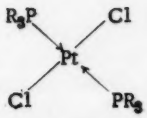
COMMUNICATION 2. COMPLEX COMPOUNDS WITH PLATINOUS SALTS

A. E. Arbuzov and V. M. Zoroastrova

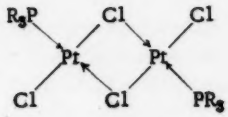
Two types of complex compound formed between tertiary phosphines and platinous salts have been prepared: simple complexes, which occur in cis and trans forms (I and II), and bridged forms, which can theoretically exist in three isomeric forms, but have been isolated up till the present time only in the trans form (III) [1,2]:



(I) (cis)



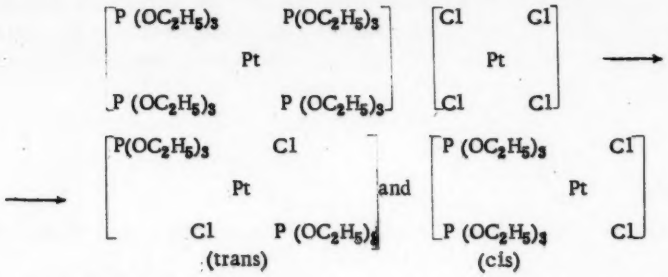
(II) (trans)



(III)

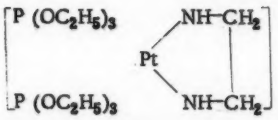
The study of the complex compounds of bivalent platinum was initiated by the work of Schutzenberger [3], Pomey [4], and Risler [5]. The physical properties of the complexes obtained remained practically without description by these authors. Rosenheim [6] attempted to isolate the isomeric compounds $PtCl_2 \cdot 2P(OC_2H_5)_3$, but succeeded in isolating only one compound, to which he arbitrarily ascribed the trans configuration. For the compound $PtCl_2 \cdot P(OC_2H_5)_3 \cdot C_6H_5NH_2$ he isolated two isomers, m.p. 147° and 108°. To the high-melting form he ascribed the trans structure, and to the low-melting form the cis structure. Rosenheim established that the compounds $PtCl_2 \cdot PCl_3$ and $PtCl_2 \cdot P(OR)_3$ have double molecules.

Considerably later, complex compounds of bivalent platinum were studied by Grinberg and Troitskaya [7]. Unlike previous investigators, Grinberg and Troitskaya prepared phosphite complexes not by the action of alcohols on $PtCl_2 \cdot PCl_3$ or $PtCl_2 \cdot 2PCl_3$, but by the reaction of triethyl phosphite with potassium chloroplatinate (II) in aqueous solution. In this way these authors prepared the compound $[Pt\{P(OC_2H_5)_3\}_4][PtCl_4]$ and a small amount of the substance $[Pt \cdot \{P(OC_2H_5)_2OH\}_2\{P(OC_2H_5)_2O\}_2]$. The first compound, when heated in chloroform, decomposed with formation of two isomers, m.p. 58-59° and 52.- 52.5°.



(trans) (cis)

On the basis of a study of the reaction of trans isomers with ethylenediamine and with ammonia, a reaction that leads in the case of the isomer of m.p. 58-59° to the products



$PtCl_4$ and $[Pt\{P(OC_2H_5)_3\}_2(NH_3)_2]Cl_2$.

Grinberg and Troitskaya assigned it the cis configuration. By the action of thiourea on the isomer of m.p. 58-59°, instead of observing the expected entry of four molecules of thiourea, they obtained a compound to which they ascribed the following structure:

$[Pt\{P(OC_2H_5)_2OH\}_2\{CS(NH_2)_2\}_2]Cl_2$.

By means of an exchange reaction between the complex $[Pt\{P(OC_2H_5)_3\}_2Cl_2]$ and potassium iodide, Grinberg and Troitskaya obtained the corresponding iodide $[Pt\{P(OC_2H_5)_3\}_2I_2]$, m.p. 85-86°. The same iodide was obtained by them by the action of potassium iodoplatinate (II) on triethyl phosphite. The authors assigned the cis configuration to the compound of m.p. 85-86°. By carrying out the last reaction in the cold, they isolated an unstable form of m.p. 39-49°, to which they assigned the trans structure.

In the present communication results are given of work on the preparation of complexes of phosphorous esters with bivalent platinum by the direct action of platinous chloride on the esters and of work on some of the reactions of these compounds. We have repeated Schutzenberger's experiments and have obtained by his method the complexes $PtCl_2 \cdot PCl_3$ (m.p. 170-173°) and $PtCl_2 \cdot 2PCl_3$ (m.p. ~160°). By the action of methanol and of ethanol on these we have obtained Schutzenberger's complexes $PtCl_2 \cdot 2P(OCH_3)_3$ and $PtCl_2 \cdot 2P(OC_2H_5)_3$, and have determined their melting points (see table). By the direct action of platinous chloride on trimethyl phosphite and on triethyl phosphite, the complexes $PtCl_2 \cdot 2P(OR)_3$ (where R = CH_3 and C_2H_5), identical with the corresponding compounds of Schutzenberger, have been prepared.

The melting points of the complex $PtCl_2 \cdot 2P(OC_2H_5)_3$, which we obtained from $PtCl_2 \cdot 2PCl_3$, and by the action of $PtCl_2$ on triethyl phosphite, was identical with that of the compound $[Pt\{P(OC_2H_5)_3\}_2Cl_2]$, obtained by Grinberg and Troitskaya from $K_2[PtCl_4]$ and $P(OC_2H_5)_3$. In the table the constants are given of other compounds of the type $PtCl_2 \cdot 2P(OR)_3$, which we obtained by the direct action of $PtCl_2$ on phosphorous esters. The complexes No. 7 and No. 8, from triisopropyl phosphite and triphenyl phosphite respectively, have not been previously described in the literature.

The molecular weight of the isopropyl ester complex determined cryoscopically and that of the phenyl ester determined by Rast's method in camphor corresponded to monomeric forms.

$PtCl_2 \cdot 2P(OC_3H_7\text{-}i)_3$. Found M 644; calculated M 682.4
$PtCl_2 \cdot 2P(OC_6H_5)_3$. Found M 868.1; calculated M 886.3

Both products consisted of colorless crystals, soluble in many organic solvents and stable to storage.

When $PtCl_2 \cdot 2P(OC_2H_5)_3$ and $PtCl_2 \cdot 2P(OC_3H_7\text{-}i)_3$ react with potassium iodide in aqueous alcohol, an exchange reaction occurs with formation of the corresponding iodides $[PtI_2 \cdot 2P(OC_2H_5)_3]$, m.p. 85-86°, and $[PtI_2 \cdot 2P(OC_3H_7\text{-}i)_3]$, m.p. 137°. The complex $[PtI_2 \cdot 2P(OC_2H_5)_3]$ was found to be identical with Grinberg and Troitskaya's complex obtained from K_2PtI_4 and $P(OC_2H_5)_3$ (mixed m.p. 85°). Somewhat unexpected results were obtained by the action on $PtCl_2 \cdot 2P(OR)_3$ (R = CH_3, C_2H_5 and $C_3H_7\text{-}i$) of thiourea under the conditions indicated by Grinberg and Troitskaya. When we investigated the products of the reaction of thiourea with the complexes indicated, we obtained results that differed from those of Grinberg and Troitskaya for the complex containing the ethyl radical. The analytical results (Pt and P) that we obtained for the three products correspond most closely to the formula:

$$\begin{bmatrix} (RO)_2POH & & CS(NH_2)_2 \\ & \cdot Pt & \\ CS(NH_2)_2 & & CS(NH_2)_2 \end{bmatrix} Cl_2,$$

where R = CH_3, C_2H_5, $C_3H_7\text{-}i$. The products obtained are crystalline substances having m.p. 150-153° (R=CH_3); m.p. 185° (R=C_2H_5) and m.p. 185-187° (R=$C_3H_7\text{-}i$), with decomposition in each case.

For the ethyl compound Grinberg and Troitskaya give the decomposition temperature as 184° and give the following analytical figures:

	Found %:	Pt 28.31; 28.68; S 9.42
$[Pt\{P(OC_2H_5)_2OH\}_2\{CS(NH_2)_2\}_2]Cl_2$.	Calculated %:	Pt 28.10; S 9.23

We have obtained the following results:

	Found %:	Pt 30.78; 30.98; P 4.44; 4.52; S 14.68; 14.59
$[Pt\{P(OC_2H_5)_2OH\}\{CS(NH_2)_2\}_3]Cl_2$.	Calculated %:	Pt 30.87; P 4.90; S 15.21

For the methyl and isopropyl compounds the analytical figures again correspond to the presence in the compounds of three molecules of thiourea. This replacement of three components of the inner zone by thiourea molecules is unusual [8], and the interesting question of the nature of the products of the action of thiourea on the complexes $[PtCl_2 \cdot 2P(OR)_3]$ requires further study.

TABLE

No.	Formula		M.p. (°C)		
			Our results	Schutzenberger's results	Grinberg and Troitskaya's results
1	$PtCl_2 \cdot PCl_3$	(yellow crystals)	170-173 (dec.)	170	–
2	$PtCl_2 \cdot 2PCl_3$	(colorless crystals)	~160	~160	–
3	$PtCl_2 \cdot P(OCH_3)_3$	(orange crystals)	131-132	–	–
4	$PtCl_2 \cdot 2P(OCH_3)_3$	(colorless crystals)	137-138	–	–
5	$PtCl_2 \cdot P(OC_2H_5)_3$	(orange-yellow)	83	80-83	–
6	$PtCl_2 \cdot 2P(OC_2H_5)_3$	(colorless crystals)	59-60	–	59-60
7	$PtCl_2 \cdot 2P(OC_3H_7\text{-}i)_3$	(colorless crystals)	132-133	–	–
8	$PtCl_2 \cdot 2P(OC_6H_5)_3$	(colorless crystals)	190-191 (dec.)	–	–

EXPERIMENTAL

1. Preparation of the Complex Compound of Platinous Chloride with Phosphorus Trichloride. A mixture of platinum black (3.6 g) and phosphorus pentachloride (3.85 g) was sealed in a glass tube and heated in a sand bath at 230° for two hours. The reaction product was extracted with dry benzene. When the greater part of the solvent had been evaporated off in a stream of dry carbon dioxide, orange needles of the complex $PtCl_2 \cdot PCl_3$ (I), m.p. 170-173° (dec.) came down. It is a very hygroscopic substance, strongly fuming in air. The product was analyzed by heating with sodium carbonate.

Found %: P 7.82; Cl 43.74

$PtCl_2 \cdot PCl_3$. Calculated %: P 7.68; Cl 43.93

2. Preparation of the Complex Compound $PtCl_2 \cdot 2PCl_3$. The compound $PtCl_2 \cdot 2PCl_3$ (II) was obtained from the preceding compound by the action of excess of phosphorus trichloride. When reaction was complete, the phosphorus trichloride was removed under reduced pressure in a stream of dry carbon dioxide. The crystalline grayish-yellow residue was recrystallized from a small amount of benzene; it melted at about 160°. This compound, like the first, is unstable in air.

3. Preparation of $PtCl_2 \cdot P(OCH_3)_3$. Anhydrous methanol (4 ml) was added to the product I (1.92 g). Reaction was accompanied by rise of temperature and evolution of hydrogen chloride. The excess of methanol and hydrogen chloride was removed under reduced pressure in an atmosphere of carbon dioxide. The residue was crystallized from dry benzene, and orange-yellow crystals (1.21 g), which melted at 131-132° with decomposition to a dark-colored liquid, were obtained. The product was soluble in ether, benzene, methanol, and ethanol, but insoluble in water; it was stable in air. It was analyzed as follows: A weighed amount of the substance was heated with concentrated nitric acid (30 drops) in a sealed tube at 200-250° for 5.5 hrs. Oxidation was then complete, and the contents of the tube were poured into a porcelain dish and evaporated on the water bath to dryness. In order to remove nitric acid completely, several additions of concentrated hydrochloric acid were made to the residue. The residue was dissolved in water (100 ml), and concentrated sulfuric and hydrochloric acids (0.3 ml of each) were added. Hydrogen sulfide was passed through the hot solution, and the black precipitate of PtS_2 was filtered off and roasted in a weighed porcelain crucible to give pure platinum. Phosphorus was determined in the filtrate from the separation of platinic sulfide: the clear colorless solution was diluted to 400 ml with water and concentrated sulfuric and nitric acids (10 ml of each) and a 50% solution of NH_4NO_3 were added. The solution was heated on a boiling water bath, and phosphorus was precipitated with ammonium molybdate.

Found %: Pt 51.07; P 8.31

$C_3H_9O_3PCl_2Pt$. Calculated %: Pt 50.03; P 7.94

4. Preparation of $PtCl_2 \cdot 2P(OCH_3)_3$. The preparation of this compound was similar to that of the previous one. The inorganic complex II (1.44 g) was treated with dry methanol. After removal of excess methanol under reduced pressure, crystals appeared. They were contaminated with a grayish incrustation and were purified by recrystallization from methanol, giving colorless crystals (0.9 g) of m.p. 137-138°. Analysis was carried out by oxidation of the substance with concentrated nitric acid in a sealed tube, the platinum being precipitated with hydrogen sulfide, and phosphorus with ammonium molybdate.

Found %: Pt 38.31; P 12.43

$C_6H_{18}O_6P_2Cl_2Pt$: Calculated %: Pt 37.96; P 12.05

The substance $PtCl_2 \cdot 2P(OCH_3)_3$ was prepared also by the action of platinous chloride on trimethyl phosphite. Platinous chloride (1.33 g) was added in small portions to a solution of trimethyl phosphite (0.62 g) in dry benzene (4 ml) (equimolecular proportions of reactants). The temperature of the mixture rose to 42-43°. The products obtained were 0.25 g of crystals, m.p. 137° (from methanol) and a substance (colorless crystals) not containing halogen, m.p. 171-172°. The structure of the latter was not established (analytical figures: Pt 32.67; P 16.90).

5. Preparation of $PtCl_2 \cdot P(OC_2H_5)_3$. This substance was prepared similarly to the trimethyl phosphite compound by the action of dry ethanol on the inorganic complex I. Unlike the methyl compound, the compound of triethyl phosphite with platinous chloride was not readily crystallized out. It forms orange-yellow crystals, m.p. 83°, which can be kept at ordinary temperature for a long time without noticeable change. On being heated to 180°, it decomposes and is converted into a dark-brown liquid.

6. Preparation of $PtCl_2 \cdot 2P(OC_2H_5)_3$. The inorganic complex II was treated with anhydrous ethanol. Hydrogen chloride and the greater part of the alcohol were removed under reduced pressure. A viscous liquid product was obtained which, after standing for several days in a desiccator over sulfuric acid, crystallized out when rubbed out with a glass rod. The product was recrystallized from aqueous alcohol to give colorless crystals, m.p. 59-60° (the recrystallization is conveniently done as follows: the product is dissolved in as little alcohol as possible, about one-third of this volume of water is added, and the mixture is cooled in snow). The compound of m.p. 59° was obtained also by the direct action of $PtCl_2$ on $P(OC_2H_5)_3$.

7. Preparation of $PtCl_2 \cdot 2P(OC_3H_7\text{-}i)_3$. The complex compound of triisopropyl phosphite with platinous chloride was prepared by the direct action of the platinum salt on the phosphorous ester.

Expt. 1. Platinous chloride (0.6 g) was added in portions to triisopropyl phosphite (0.47 g, i.e., one mole per mole of $PtCl_2$). Dissolution of the salt was accompanied by rise in the temperature of the mixture to 50°. The reaction product was dissolved in absolute methanol (5 ml) and separated from the unchanged $PtCl_2$ (0.23 g). Faintly colored crystals (dirty pink) came down on standing. After a second crystallization from methanol containing animal charcoal, a colorless substance, m.p. 132-133° was obtained; it was soluble in benzene, ether, methanol, and ethanol, but was difficultly soluble in water. Analysis for Pt (oxidation with concentrated nitric acid and precipitation with hydrogen sulfide) gave a result corresponding to the formula $PtCl_2 \cdot 2P(OC_3H_7\text{-}i)_3$.

Found %: Pt 28.56; P 9.25

$C_{18}H_{42}O_6P_2PtCl_2$. Calculated %: Pt 28.60; P 9.08

Expt. 2. Platinous chloride (0.67 g) was added in small portions to triisopropyl phosphite (1.04 g, i.e. two moles per mole of platinum salt) diluted with a small amount of dry benzene. The addition of each portion was accompanied by evolution of heat with rise in temperature to 50° or somewhat higher. A crystalline product m.p. 132-133° was obtained from methanol. Its molecular weight in benzene solution was determined cryoscopically.

Found: M 644; $C_{18}H_{42}O_6P_2PtCl_2$. Calculated: M 682.47.

8. Preparation of $PtCl_2 \cdot 2P(OC_6H_5)_3$. Platinous chloride (0.24 g) was added to a solution of freshly distilled triphenyl phosphite (0.6 g, i.e. two moles per mole of platinum salt) in dry benzene (2 ml). The mixture was heated cautiously until the salt was almost completely dissolved. When the benzene solution was cooled, fine glistening crystals, m.p. 186-189° (dec) came down. Recrystallization from benzene yielded well formed, colorless prisms, (0.28 g) m.p. 190-191° (dec.). The product was readily soluble in acetone, hot alcohol, hot benzene, and dioxane; it was poorly soluble in ether and insoluble in water.

Found %: Pt 21.74

$C_{18}H_{30}O_6P_2PtCl_2$. Calculated %: Pt 22.02

It was found in a separate experiment that a product of the same composition is formed by mixing equimolecular proportions of $PtCl_2$ and triphenyl phosphite. The molecular weight of the product was determined by Rast's method.

Found: M 868.1

$C_{36}H_{30}O_6P_2PtCl_2$ Calculated: M 886.39

Attempts to determine the molecular weight cryoscopically in benzene or dioxane were not successful owing to the sharp reduction in the solubility of the product on cooling (during the determination, the substance crystallized out from the solution).

9. Reaction of $PtCl_2 \cdot 2P(OCH_3)_3$ with potassium iodide. A solution of potassium iodide (0.17 g) in water (1 ml) was added dropwise to a warm solution prepared by heating the compound $PtCl_2 \cdot 2P(OCH_3)_3$ (0.5 g) with methanol (4 ml). The addition of each drop was accompanied by separation of some yellow precipitate. The product obtained (0.6 g) melted, after crystallization from alcohol, at 145-147° (dec.); it consisted of light-yellow crystals, soluble in hot alcohol, in acetone, and in benzene, not very soluble in ether, and insoluble in water.

Found %: Pt 27.88; P 8.90

$C_6H_{18}O_6PtI_2$. Calculated %: Pt 28.00; P 8.89

10. Reaction of $PtCl_2 \cdot 2P(OC_2H_5)_3$ with potassium iodide. The compound of m.p. 59-60° (0.3 g) was dissolved in ethanol (3 ml). To this alcoholic solution, an aqueous solution of potassium iodide (0.26 g) was added, and a yellow precipitate formed immediately. It was filtered off and recrystallized from alcohol (this compound, like the complex compound of trimethyl phosphite with PtI_2, is much more soluble in hot alcohol than in cold). The substance obtained (0.3 g) melted at 85-86° to a yellow liquid. When mixed with Troitskaya's product [9] it melted at 85°. It was of good solubility in benzene, acetone, and ether, but was insoluble in water.

Found %: Pt 24.58; P 7.84

$C_{12}H_{30}O_6P_2PtI_2$, Calculated %: Pt 24.96; P 7.93

11. Reaction of $PtCl_2 \cdot 2P(OC_3H_7\text{-}i)_3$ with potassium iodide. To a solution of $PtCl_2 \cdot 2P(OC_3H_7\text{-}i)_3$ (0.1 g) in absolute methanol (3 ml), a solution of potassium iodide (0.09 g) in water (7 ml) was added drop by drop. With the addition of the first few drops the solution turned yellow, and further additions led to the appearance of yellow crystals. When the whole of the potassium iodide solution had been added, the yellow product was filtered off and recrystallized from methanol. The substance obtained (0.1 g) melted at 137° and was similar in properties to the analogous triethyl phosphite compound.

Found %: Pt 22.80; P 7.07

$C_{18}H_{42}O_6P_2PtI_2$. Calculated %: Pt 22.56; P 7.00

12. Reaction of $PtCl_2 \cdot 2P(OCH_3)_3$ with thiourea. A mixture of the complex (0.55 g) and thiourea (0.65 g) was dissolved in water (3 ml). Concentrated hydrochloric acid was added, and a colorless crystalline precipitate rapidly made its apperance. It was filtered off (0.11 g) and found to have an indefinite melting point: 105-120° with decomposition. After some time, a second crop of crystals was obtained. This product was yellowish in color and, after crystallization from hydrochloric acid, it melted with decomposition at 150-153°, forming a yellow liquid. A yield of 0.15 g* was obtained.

Found %: Pt 32.46; P 4.79

$C_5H_{19}O_3PPtCl_2S_3N_6$. Calculated %: Pt 32.29; P 5.12

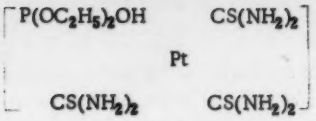
13. Reaction of $PtCl_2 \cdot 2P(OC_2H_5)_3$ with thiourea. Concentrated hydrochloric acid was added to a solution of $PtCl_2 \cdot 2P(OC_2H_5)_3$ (0.9 g) and thiourea (2.7 g) in water (10 ml). After 15-20 minutes, colorless needlelike crystals began to precipitate from the solution. They were filtered off (0.6 g). The substance was twice reprecipitated with ether from its solution in methanol. It melted at about 185° with considerable decomposition; on melting, it became bright yellow in color. The substance was not soluble in ether, benzene, or acetone; it was of low solubility in water, but dissolved in methanol.

$$\begin{bmatrix} P(OC_2H_5)_3 & CS(NH_2)_2 \\ & Pt \\ CS(NH_2)_2 & CS(NH_2)_2 \end{bmatrix} Cl_2.$$

Found %: Pt 30.78; 30.98; P 4.44; 4.52; S 14.68; 14.59

Calculated %: Pt 29.55; P 4.69; S 14.54

* The low yield of the product arises from its high solubility in water.



Cl_2. Calculated %: Pt 30.87; P 4.90; S 15.26

14. Reaction of $PtCl_2 \cdot 2P(OC_3H_7\text{-}i)_3$ with thiourea. The product of m.p. 132-133° (0.17 g) and thiourea (0.3 g) were dissolved in water (5 ml). To the colorless solution obtained, ten drops of concentrated hydrochloric acid were added. The solution was shaken, and a white crystalline precipitate (0.14 g) soon began to make its appearance. The product was similar in outward appearance and other properties (solubility, effect of heat) to the corresponding ethyl compound. On being heated to 185-187°, it melted with much frothing to a yellow liquid.

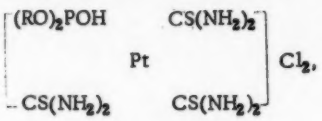
	Found %:	Pt 28.42; 28.23;	P 4.49; 4.83
$C_{12}H_{33}O_3PPtS_3N_6Cl_2$.	Calculated %:	Pt 27.78;	P 4.41
$C_9H_{27}O_3PPtS_3N_6Cl_2$.	Calculated %:	Pt 29.55;	P 4.69

SUMMARY

1. Compounds of the general formula $PtCl_2 \cdot 2P(OR)_3$, where R = CH_3, C_2H_5, C_3H_7-i, and C_6H_5, have been prepared by the action of platinous chloride on trialkyl phosphites, and some of their properties have been studied. The methyl and ethyl compounds were found to be identical with the complexes obtained by the action of methanol and ethanol respectively on $PtCl_2 \cdot 2PCl_3$.

2. By means of an exchange reaction with potassium iodide, $PtCl_2 \cdot 2P(OC_2H_5)_3$ and $PtCl_2 \cdot 2P(OC_3H_7\text{-}i)_3$ have been converted into the corresponding iodides.

3. By the action of thiourea on the complexes $PtCl_2 \cdot 2P(OR)_3$ (where R = CH_3; C_2H_5; C_3H_7-i), crystalline compounds have been prepared which correspond in their analyses to:



where R = CH_3; C_2H_5 and C_3H_7-i.

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LITERATURE CITED

[1] A. E. Arbuzov and V. M. Zoroastrova, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 5, 809 (1952).*

[2] K. A. Jensen, Z. anorg. Chem. 229, 250 (1936); J. Chatt, J. Chem. Soc. 2301 (1950); ibid. 652 (1952).

[3] P. Schutzenberger, Bull. Soc. chim. 17, 482 (1872); 18, 101, 144 (1872).

[4] E. M. Pomey, Bull. Soc. chim. 35, 420 (1881).

[5] M. Risler, Bull. Soc. chim. 18, 151(1872).

[6] A. Rosenheim and W. Loewenstamm, Z. anorg. Chem. 37, 394 (1903); A. Rosenheim and W. Lewy, Z. anorg. Chem. 43, 41 (1905).

[7] A. A. Grinberg and A. D. Troitskaya, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 4, 178 (1944).

[8] N. S. Kurnakov, J. Russ. Phys. Chem. Soc. 25, 565 (1893); A. A. Grinberg and Z. A. Razumova, J. Gen. Chem. 18, 282 (1948).

[9] A. D. Troitskaya, Dissertation, Kazan, 1944.

*See Consultants Bureau translation, p. 729.

COMPLEX COMPOUNDS OF PHOSPHOROUS ESTERS

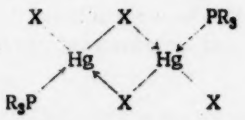
COMMUNICATION 3. COMPLEX COMPOUNDS WITH MERCURY SALTS

A. E. Arbuzov and V. M. Zoroastrova

Tertiary phosphines form a series of complex compounds with the halides of bivalent mercury [1]. The following types of complex have been described [2]:

A) $[(R_3P)_2 \cdot HgX_2]$. This type is given by triarylphosphines, but not by trialkylphosphines.

B) $[(R_3P)_2 \cdot (HgX_2)_2]$. In the literature, many compounds of this type are described as having the formula $R_3P \cdot HgX_2$. Evans, Mann, Peiser, and Purdie [2] showed that the molecule was double and had a bridged structure, and they considered that it probably had a tetrahedral configuration, the four groups being tetrahedrally arranged around the mercury atoms in the transposition:



$[(C_2H_5)_3P_2(HgI_2)]$ was obtained as colorless crystals, the propyl homolog was obtained both as colorless and as yellow crystals, and the butyl and amyl derivatives were obtained only in the yellow form.

The following further types of mercury complex are known:

C) $[(R_3P)_2(HgX_2)_3]$.
D) $[(R_3P)_2(HgX_2)_4]$.
E) $[(R_3P)_3(HgX_2)_2]$.

We have not found any data in the literature concerning complex compounds formed between full phosphorous esters and mercury halides, and we were therefore prompted to prepare such complex compounds with the object of comparing them with the phosphine complexes. We have investigated the action of mercuric chloride, bromide, and iodide on the trimethyl, triethyl, tripropyl, triisopropyl, and triphenyl esters of phosphorous acid, and have found that these mercuric halides react with the indicated esters with rise in temperature, though the triphenyl ester reacts less vigorously than the others.

Addition of one mole of mercuric salt to one mole or two moles of ester yielded products corresponding to the combination of equimolecular amounts of ester and mercury salt. The propyl and phenyl compounds were obtained in the form of thick syrups. Determination of the molecular weights by cryoscopy in benzene gave values corresponding to double molecules. Thus, the mercury complex compounds that we have prepared correspond to the phosphine complexes of type B. The physical properties of the compounds obtained are given below in a table.

All the compounds listed in the table are of low stability: they rapidly decompose on standing in air. The chloride compounds are the most stable, and the iodide compounds are the least stable. All the crystalline compounds obtained are colorless, except $[P(OC_3H_{7\text{-}i})_3HgI_2]_2$, the crystals of which are yellow. In the preparation of the complexes $[(C_2H_5O)_3P \cdot HgCl_2]_2$ and $[(CH_3O)_3P \cdot HgCl_2]_2$, very small amounts of crystalline products having m. p. 93-96° and 114° respectively were isolated; these corresponded in phosphorus content to $(C_2H_5O)_3P \cdot 2HgCl_2$ and $(CH_3O)_3P \cdot 2HgCl_2$, respectively. It is probable that these compounds correspond in type to the type-D phosphine complexes $[(R_3P)_2(HgX_2)_4]$ but in view of the small amounts available they were not investigated further.

EXPERIMENTAL

1. Reaction of $HgCl_2$ with Trimethyl Phosphite.

Mercuric chloride (1.87 g) was added in portions to trimethyl phosphite (0.85 g, i.e., one mole per mole of

TABLE

No.	Formula	M.p. (°C)	Mol. weight	
			Found	Calculated for double formula
1	$[HgBr_2 \cdot P(OCH_3)_3]_2$, colorless cryst.	107-109	–	–
2	$[HgCl_2 \cdot P(OC_2H_5)_3]_2$, colorless cryst.	73-75 (dec.)	812.9	875.28
3	$[HgBr_2 \cdot P(OC_2H_5)_3]_2$, colorless cryst.	67-73 (dec.)	–	–
4	$[HgCl_2 \cdot P(OC_3H_{7-i})_3]_2$, colorless cryst.	117-118 (dec.)	895	959.3
5	$[HgBr_2 \cdot P(OC_3H_{7-i})_3]_2$, colorless cryst.	128-130 (dec.)	1031.2	1137.1
6	$[HgI_2 \cdot P(OC_3H_{7-i})_3]_2$, yellow cryst.	~120 (yellow cryst.)	–	–
7	$HgCl_2 \cdot P(OC_3H_7)_3$	thick liquids		
8	$HgBr_2 \cdot P(OC_3H_7)_3$			
9	$HgCl_2 \cdot (OC_6H_5)_3$	thick liquids		
10	$HgBr_2 \cdot P(OC_6H_5)_3$			

mercuric chloride). The dissolution of the salt was accompanied by evolution of heat; it did not dissolve completely. The reaction product was treated with 5 ml of dry ether (and the amount of precipitate increased). On evaporation of the ether, a small quantity of crystals, m.p. 78-84° (dec.) came down. The crystals very rapidly underwent change, forming into an oily spot on the filter paper. The product was not analyzed owing to the small amount available. The precipitate that remained after treatment of the reaction product with ether was extracted with benzene. A small quantity of colorless crystals, which melted with considerable decomposition at 114°, were obtained, and analysis for phosphorus indicated that they were composed of the addition product of two molecules of mercuric chloride with one molecule of trimethyl phosphite.

Found %: P 4.20

$C_3H_9O_3PHg_2Cl_4$. Calculated %: P 4.64

The product decomposed when left in a desiccator for four days. When heated to 240° it did not melt, but gradually sintered together.

2. Reaction of $HgBr_2$ with Trimethyl Phosphite.

Mercuric bromide (2.5 g) was added in portions to trimethyl phosphite (0.88 g). Reaction set in, the temperature rising to 53-55°. Part of the salt remained undissolved in the trimethyl phosphite. The reaction mixture was treated with a mixture of benzene and ether. A product (0.98 g) consisting of colorless prisms, m.p. 107-109° (dec.) was obtained.

Found %: P 6.52

$C_3H_9O_3PHgBr_2$. Calculated %: P 6.40

Attempts to determine the molecular weight of the product in benzene and in dioxane solution failed owing to the low solubility of the material, which crystallized out during the cooling.

3. Preparation of $HgCl_2 \cdot P(OC_2H_5)_3$

Mercuric chloride (2.44 g) was added in three portions to triethyl phosphite (1.5 g, i.e., one mole per mole of mercuric salt). With each addition, the temperature of the mixture rose to 50-53°. Scratching with a glass rod caused the reaction mass to solidify rapidly. The reaction products were extracted with a mixture of ether and benzene, giving a solution from which, on cooling, large needlelike crystals came down. The melting point after two recrystallizations was 73-75°, and the yield was 1.23 g. The portion of the reaction products that did not dissolve in the ether-benzene mixture was treated with hot benzene. When the benzene was cooled, a small quantity of crystals, m.p. 93-96° (dec.) was obtained.

Analysis of the product of m.p. 73-75°:

Found %: P 7.27; 7.00

$HgCl_2 \cdot P(OC_2H_5)_3$. Calculated %: P 7.08

Molecular weight determination:

	Found:	M 812.9	(cryoscopic
$HgCl_2 \cdot P(OC_2H_5)_3$.	Calculated:	M 437.64	method in
$[HgCl_2 \cdot P(OC_2H_5)_3]_2$.	Calculated:	M 875.28	benzene solution)

Analysis of the product of m.p. 93-96°

	Found %:	P 4.43; 4.41
$P(OC_2H_5)_2 \cdot HgCl_2 \cdot HgCl_2$.	Calculated %:	P 4.38

Owing to the small amount available of this substance, its molecular weight was not determined.

4. Preparation of $HgBr_2 \cdot P(OC_2H_5)_3$

The triethyl phosphite-mercuric bromide compound was prepared similarly to the previous product from 1.8 g of $HgBr_2$ and 0.8 g of the ester. Again the reaction was accompanied by evolution of heat. The solid product obtained was treated with dry ether. Some glistening crystals were isolated, but on standing in air they rapidly became dull, leaving an oily patch on the filter paper. They did not melt sharply (69-73°) (from benzene and heptane).

	Found %:	P 5.80; 5.99
$HgBr_2 \cdot P(OC_2H_5)_3$.	Calculated %:	P 5.89

5. Reaction of $HgCl_2$ with Triisopropyl Phosphite.

Expt. 1. For each mole of the ester, one mole of mercuric chloride was taken: Mercuric chloride (1.4 g) was added in small portions to triisopropyl phosphite (1 g). The mercuric chloride dissolved in the ester with rise in temperature to 42-44°. The reaction product, a gray solid mass, was extracted with benzene and then precipitated from solution by means of ligroin. The product (colorless prisms) melted, after recrystallization from methanol, at 117-118° (dec.), forming a colorless liquid, which foamed strongly and then turned milky. The product was soluble in organic solvents, but insoluble in water.

	Found %:	Hg 40.78; P 6.52; 6.56;	Cl 15.07
$HgCl_2 \cdot P(OC_3H_7)_3$.	Calculated %:	Hg 41.18; P 6.46;	Cl 14.79

	Found:	M 895	(cryoscopic
$HgCl_2 \cdot P(OC_3H_7\text{-}i)_3$	Calculated:	M 479.68	method in
$[HgCl_2 \cdot P(OC_3H_7\text{-}i)_3]_2$.	Calculated:	M 959.36	benzene solution)

Expt. 2. Two moles of ester were taken per mole of mercuric chloride, and, after similar treatment, a product of m.p. 117-118° was isolated.

6. Reaction of $HgBr_2$ with Triisopropyl Phosphite

Mercuric bromide (1.4 g) was added in portions to triisopropyl phosphite (1.5 g). With each addition the temperature of the mixture rose to 52-55°. The reaction mixture solidified on cooling, and the product was recrystallized several times from a mixture of benzene and heptane, giving well formed, colorless prisms (0.85 g), melting with decomposition at 128-130°. It was similar in appearance to the chloride compound, but was more stable. It rapidly decomposed on standing in the air (the compound $HgBr_2 \cdot P(OC_3H_7\text{-}i)_3$ could not be recrystallized from methanol), and it was considerably more soluble than the chloride compound in ether.

	Found %:	P 5.30
$HgBr_2 \cdot P(OC_3H_{7\text{-}i})_3$.	Calculated %:	P 5.44

	Found:	M 1031.2	(cryoscopic
$[HgBr_2 \cdot P(OC_3H_7\text{-}i)_3]$.	Calculated:	M 568.59	method in
$[HgBr_2 \cdot P(OC_3H_{7\text{-}i})_3]_2$.	Calculated:	M 1137.1	benzene solution)

The product of m.p. 128-130° was prepared also by mixing one molecular proportion of $HgBr_2$ with two of triisopropyl phosphite.

7. Reaction of HgI_2 with $P(OC_3H_7\text{-}i)_3$

Mercuric iodide (0.9 g) was added gradually to triisopropyl phosphite (0.4 g, i.e., one mole per mole of

mercury salt). The HgI_2 dissolved in the ester with rise of temperature (to 40°) and formation of a colorless solution, which, on being stirred with a glass rod, rapidly crystallized, forming a yellowish mass of crystals. The reaction product was dissolved in benzene, and a small amount of unchanged mercury salt was removed by filtration. Rapid evaporation of the benzene and addition of heptane led to separation of lemon-yellow needles. When heated to 120°, the product decomposed with separation of brownish material. On standing in the air the crystals changed in color, within 30 minutes of the completion of the synthesis, from lemon yellow to orange. The molecular weight of the compound was not determined owing to its instability.

Found %: P 4.40

$HgI_2 \cdot P(OC_3H_7\text{-}i)_3$. Calculated %: P 4.67

The phenyl ester of phosphorous acid reacted very feebly with $HgCl_2$ and $HgBr_2$. After the usual solvent treatments, attempts to isolate crystalline compounds failed.

The n-propyl ester of phosphorous acid reacted very vigorously with $HgCl_2$ and $HgBr_2$, but the reaction products did not crystallize, but remained in the form of a thick syrup.

SUMMARY

1. It has been found that mercuric halides react with full esters of phosphorous acid with formation of complex compounds. The following compounds have been isolated in the crystalline form:

$[HgBr_2 \cdot P(OCH_3)_3]_2$; $[HgCl_2 \cdot P(OC_2H_5)_3]_2$.
$[HgBr_2 \cdot P(OC_2H_5)_3]_2$; $[HgCl_2 \cdot P(OC_3H_7\text{-}i)_3]_2$.
$[HgBr_2 \cdot P(OC_3H_7\text{-}i)_3]_2$; $[HgI_2 \cdot P(OC_3H_7\text{-}i)_3]_2$.

2. Molecular weight determinations by cryoscopy in benzene on the compounds formed showed that their molecules are dimeric.

3. The complex compounds obtained, complexes of mercuric halides with trialkyl phosphites $[(RO)_3P \cdot HgX_2]_2$, are analogs of the corresponding phosphine complexes $[R_3P \cdot HgX_2]_2$, and they belong to the bridged type.

LITERATURE CITED

[1] A. E. Arbuzov and V. M. Zoroastrova, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., No. 5, 818 (1952)*

[2] R. C. Evans, F. G. Mann, H. S. Peiser and D. Purdie, J. Chem. Soc. 1209 (1940).

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* See Consultants Bureau translation, p. 737.

THE TAUTOMERISM OF CARBOSTYRIL DERIVATIVES

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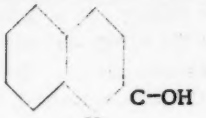
The discovery of the tautomerism of carbostyril derivatives is of long standing, being comparable in this respect to similar discoveries concerning the tautomerism of acetoacetic ester and isatin, and the behavior of carbostyril and its derivatives is regarded as a classical, deeply studied example of tautomeric phenomena. However, examination of the literature shows that the question of the tautomerism of carbostyril and its derivatives has not, in fact, received adequate study [1, 3, 4], and the structure of carbostyril, as also that of isatin, cannot be considered to be unequivocally established.

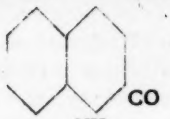
In our previous communication [2], the tautomerism of isatin derivatives was considered, and the main questions that arose – which concerned the structures of the tautomeric compounds themselves, the structures of their metal derivatives, and the double-decomposition reactions of the metal derivatives of the tautomers with halogen compounds – may be associated in equal measure with carbostyril derivatives. The only difference is that the matter is still more complicated for carbostyril.

The establishment of the existence of two series of derivatives, regarded as O- and N-derivatives, occurred somewhat later (in 1887) for carbostyril than for isatin [4]. Whereas the action of methyl (or ethyl) iodide on the silver salt leads to the formation of the O-methyl (or O-ethyl) ether, reaction of these halides with alkaline solution of carbostyril gives N- and O-alkyl-substituted carbostyrils in various relative amounts, depending on the reaction conditions.

Carbostyril itself, as also isatin, has been obtained only in one form, but, since it forms two series of derivatives, regarded as O- and N-derivatives, it may be assigned two formulas, I and II:



(I)



(II)

The structures of the alkyl esters of carbostyril were established on the basis of hydrolysis reactions, it being shown that some of these esters, the N-derivatives, were stable to the action of dilute mineral acids, whereas others, the O-derivatives, were hydrolyzed with formation of carbostyril; also, the latter are converted into N-derivatives by treatment with alkyl halide.

In the present communication, results are given of a study of double-decomposition reactions of the sodium, potassium and silver salts of carbostyril with certain halogen compounds, including halogen-substituted ethers. The alkali salts of carbostyril were prepared by the action of metallic sodium on a solution of carbostyril in freshly prepared absolute alcohol, and the silver salt was prepared from a 1% aqueous solution of carbostyril and silver nitrate solution by addition of ammonia. The salts were preserved in a desiccator, and, before being used for the reaction, the alkali salts were given a careful supplementary drying treatment. A study was made of the reactions of the carbostyril salts with the following aralkyl halides, which were prepared by the usual methods: benzyl bromide and chloride, α-bromo-p-xylene, bromotriphenylmethane, and chlorotriphenylmethane.

The reactions with the following halogen-substituted ethers were studied also: bromomethyl methyl ether, chloromethyl methyl ether, bromomethyl ethyl ether, chloromethyl ethyl ether, bromomethyl propyl ether, and chloromethyl propyl ether. All the starting materials were taken in a freshly prepared condition for reaction. The reactions were carried out in a medium of dry ether or of benzene under varying conditions of temperature: normal temperature, at the boiling point of the solvent, or at higher temperature in a sealed tube.

By the action of bromomethyl methyl ether and of chloromethyl methyl ether on the silver salt of

carbostyril, and carbostyril methoxymethyl ether, m.p. 66-67°, was isolated in each case; by the action on the silver salt of the bromomethyl and of the chloromethyl ethyl ethers, a carbostyril ethoxymethyl ether, m.p. 39-40°, was isolated; and from the bromomethyl and chloromethyl propyl ethers and the silver salt, a carbostyril propoxymethyl ether, b.p. 192-193°/12 mm, was isolated. Experiments carried out with bromomethyl and chloromethyl methyl ethers and the potassium and sodium salts of carbostyril did not lead to the preparation of a carbostyril methoxymethyl ether; carbostyril itself was obtained in all cases, owing, probably, to the exceptional readiness with which the ether obtained is hydrolyzed.

The methoxymethyl and ethoxymethyl ethers of carbostyril consist of white, well formed, needlelike crystals, but the propoxymethyl ether is a colorless liquid. All the compounds are of good solubility in ether and in benzene.

Hydrolysis of carbostyril methoxymethyl ether in caustic potash solution at the boil for one hour led to formation of carbostyril (in almost theoretical yield) and formaldehyde, which was detected by a qualitative reaction.

Attempts to hydrolyze the ethoxymethyl and propoxymethyl ethers of carbostyril in a 10% solution of caustic alkali gave negative results: the substances remained unchanged. By heating bromomethyl methyl ether with carbostyril methoxymethyl ether, a high-melting product was obtained. An attempt to hydrolyze carbostyril propoxymethyl ether in a 10% solution of hydrochloric acid also gave a negative result. The propoxymethyl ether, on being heated at 140-150° for two hours, yielded a high-melting product.

By the action of bromotriphenylmethane and of chlorotriphenylmethane on the silver and sodium salts of carbostyril, the same product was obtained in all cases: (triphenylmethyl)carbostyril, m.p. 180-181°, in the form of colorless crystals, readily soluble in ether and in benzene.

Hydrolysis of (triphenylmethyl)carbostyril in caustic potash solution yielded carbostyril and triphenylmethanol in almost quantitative yield.

By the action of benzyl bromide and of benzyl chloride on the silver salt and on the sodium salt of carbostyril, different substances were obtained (judging from their melting points). Thus, by the action of these halogen compounds on the silver salt of carbostyril, a benzylcarbostyril, of m.p. 50-51° was obtained, whereas by their action on the sodium or potassium salt a benzylcarbostyril of m.p. 95-96° was formed.

By the action of α-bromo-p-xylene on the silver salt and on the sodium salt of carbostyril, (p-tolylmethyl) carbostyrils of different melting points were obtained, as in the case of the benzyl compounds. By the action of α-bromo-p-xylene on the silver salt of carbostyril, a (p-tolylmethyl)carbostyril of m.p. 71-72° was obtained, and by its action on the sodium salt a (p-tolylmethyl)carbostyril of m.p. 131-132° was formed. Both benzylcarbostyrils and also both (p-tolylmethyl)carbostyrils were found to be very stable compounds and were not hydrolyzed when heated with 10% caustic alkali solution; on the other hand, when heated with 10% acid, the benzylcarbostyril and (p-tolylmethyl)carbostyril that had been prepared from the silver salt of carbostyril were hydrolyzed with formation of carbostyril.

The benzylcarbostyril and (p-tolylmethyl)carbostyril that were prepared from the silver salt of carbostyril and had the lower melting points (51° and 72°) are converted by being heated with benzyl bromide and α-bromp-xylene respectively into the corresponding compounds of higher melting point (96° and 132°).

Since the benzyl and p-tolylmethyl ethers of carbostyril have each been obtained in two forms, one of which may be converted into the other, their molecular weights were determined. The estimation was done by Rast's method, and it gave values corresponding to monomolecular products.

EXPERIMENTAL

Preparation of Carbostyril Methoxymethyl Ether

Action of bromomethyl methyl ether on the silver salt of carbostyril. The silver salt of carbostyril (1.26 g) was added to a solution of bromomethyl methyl ether (0.95 g) in dry ether (15 ml). Reaction set in very quickly and proceeded with evolution of heat (the ether boiled). After 30 minutes the solution was filtered and the residue was washed with dry ether. When the ether had been driven off, a thick, oily liquid remained, and this was distilled under a pressure of 17 mm Hg (b.p. 172-175°). The substance obtained (0.7 g, 50%) crystallized after standing for some time yielding white needles of m.p. 66-67°.

In a second experiment 1.25 g of bromomethyl methyl ether and 2.52 g of the silver salt were taken, and

the reaction was carried out in a dry benzene medium, the mixture being heated for 30 minutes at the boil. A white substance (1.73 g, 90.1%) in the form of small needles separated from the benzene solution; it melted at 66-67°.

Analysis of the substance of m.p. 66-67°:

Found %: N 7.66

$C_{11}H_{11}NO_2$. Calculated %: N 7.41

The methoxymethyl ether has a pleasant odor and is of good solubility in ether, benzene, and alcohol.

Action of chloromethyl methyl ether on the silver salt of carbostyril. The silver salt of carbostyril (2.52 g) was added to a solution of chloromethyl methyl ether (0.81 g) in dry benzene (15 ml). The reaction was carried out at the boiling point of benzene. After separation of silver chloride, the benzene solution was placed under vacuum. The residual oily liquid crystallized out when cooled with snow. The product (1.28 g, 68%) melted at 66-67°.

Found %: N 7.69

$C_{11}H_{11}NO_2$. Calculated %: N 7.41

Action of bromomethyl methyl ether on the sodium salt of carbostyril. Experiments were carried out under various conditions: at the boiling point of benzene, in a sealed tube heated in a boiling water bath, in a sealed tube at 110-115°, and in a sealed tube at 140-150°. The sodium salt used was carefully dried prior to the reaction. In no case was a carbostyril methoxymethyl ether isolated, but carbostyril was obtained, either in traces, or in larger amount.

The materials sealed in the tube were: bromomethyl methyl ether (1.25 g), dry benzene (10 ml), and the sodium salt (1.67 g). Heating was carried out at 110-115°. From the benzene solution, 0.9 g of carbostyril, m.p. 198-199°, was obtained.

Action of bromomethyl methyl ether on the potassium salt of carbostyril. Two experiments, at the boiling point of benzene and at 110-115°, were carried out. In each experiment carbostyril was obtained.

The flask contained bromomethyl methyl ether (1.25 g), dry benzene (15 ml), and the potassium salt (1.93 g). Reaction set in fairly quickly and proceeded with evolution of heat (the temperature rose to 40°). The mixture was boiled on the bath for 30 minutes and was filtered while still hot, the residue being washed by warming with dry benzene. The amount of potassium bromide obtained was 1.08 g (calculated amount: 1.09 g). The benzene solution yielded 1.36 g of a substance of m.p. 194-196° which melted after recrystallization from alcohol at 198-199° (i.e., it was carbostyril).

Bromomethyl methyl ether (1.25 g), dry benzene (10 ml), and the potassium salt (1.93 g) were heated together in a sealed tube at 110-115° for one hour. Carbostyril (0.82 g), m.p. 198-199°, was isolated from the benzene solution.

Preparation of Carbostyril Ethoxymethyl Ether

Action of bromomethyl ethyl ether on the silver salt of carbostyril. The silver salt of carbostyril (1.26 g) was added to a solution of bromomethyl ethyl ether (1.38 g) in dry ether (20 ml). Reaction set in very rapidly, heat being evolved (the ether boiled). The reaction mixture was boiled for 30 minutes and then filtered under suction, the residue being washed several times with dry ether. The ether was driven off,, and a precipitate (1.1 g) formed in the solution. It was treated with water (20 ml), and part of it remained undissolved as an oil at the bottom of the flask. When the mixture was filtered , the oily part remained on the filter paper; it gave a negative result in Beilstein's test for halogen. The oil was transferred to a watch glass and, after two hours, needlelike crystals (0.12 g) of m.p. 39° separated out in fan formation. The oil remaining on the filter paper was extracted with ether, and from the ethereal solution a further 0.32 g of substance of m.p. 39.5-40° was isolated. The total yield was therefore 0.5 g (50%). The substance obtained was of good solubility in ether, benzene, and alcohol, but was insoluble in water.

Found %: N 7.92

$C_{12}H_{13}ON$. Calculated %: N 7.48

Action of chloromethyl ethyl ether on the silver salt of carbostyril. The silver salt (0.9 g) was added to a solution of chloromethyl ethyl ether (0.4 g) in dry benzene (15 ml). Reaction set in and was accompanied by

some evolution of heat, the temperature rising nearly to the boiling point of benzene. The mixture was heated at the boiling point of benzene for 30 minutes, and the solution was then filtered off under suction. A viscous liquid (0.9 g) remained after removal of the benzene; it was poured onto a watch glass, which was placed on snow. After one day the substance began to crystallize; the crystals that separated were pressed off between filter papers, and 0.4 g (56%) of a substance of m.p. 39-39.5 ° was obtained. In admixture with the substance obtained by the reaction of bromomethyl ethyl ether with the silver salt of carbostyril, it melted at 38.5-39.5°.

Found %: N 6.89
$C_{12}H_{13}ON$. Calculated %: N 7.48

Found %: N 7.15
$C_{12}H_{13}ON$. Calculated %: N 7.48

Preparation of Carbostyril Propoxymethyl Ether

Action of bromomethyl propyl ether on the silver salt of carbostyril. The silver salt (2.52 g) was added to bromomethyl propyl ether (1.52 g) dissolved in dry ether (15 ml). Reaction set in very quickly, and it proceeded with evolution of heat (the ether boiled). The reaction mixture was heated at the boiling point of ether (on a water bath) for 30 minutes, and the solution was then filtered off under suction. In the distillation flask, after the ether had been driven off, there remained a viscous liquid, which was vacuum-distilled (b.p. 192-193°/12 mm in this and also in a further distillation). It had a sharp odor, similar to that of the substance obtained by reaction with chloromethyl propyl ether. The substances obtained in the reactions of the silver salt of carbostyril with bromomethyl and with chloromethyl propyl ether were united and distilled. The boiling point of the mixture was not lower than that of its components.

Found %: N 6.90
$C_{13}H_{15}ON$. Calculated %: N 6.96

Action of chloromethyl propyl ether on the silver salt of carbostyril. The silver salt (2.27 g) was added to a solution of chloromethyl propyl ether (1.0 g) in dry benzene (15 ml). Reaction started when the mixture was heated to boiling, and heating was continued at this temperature for 45 minutes. The benzene solution was distilled, and a viscous liquid remained, which distilled over at 196-197° under 15 mm pressure. The yield was 0.95 g (calculated amount: 1.92 g). The substance had a sharp characteristic odor.

Found %: N 6.78
$C_{13}H_{15}ON$. Calculated %: N 6.96

Preparation of (Triphenylmethyl) carbostyril

Action of bromotriphenylmethane on the silver salt of carbostyril. The silver salt of carbostyril (1.26 g) was added to a solution of bromotriphenylmethane (1.6 g) in dry benzene (15 ml). Reaction set in very quickly. A white crystalline substance (1.9 g) of m.p. 176-178° separated from the benzene solution when a part of the solvent had been driven off. After recrystallization from dry benzene, the substance melted at 180-181°.

Found %: N 3.69
$C_{28}H_{21}ON$. Calculated %: N 3.62

Action of chlorotriphenylmethane on the silver salt of carbostyril. The silver salt of carbostyril (1.26 g) was added to a solution of chlorotriphenylmethane (1.39 g) in dry benzene (15 ml). The mixture was maintained at its boiling point during the reaction. Crystals of m.p. 167-171° separated from the benzene solution; after several recrystallizations they melted at 180-181°. In admixture with those obtained in the preceding experiment, they melted at 180-181.5°.

Found %: N 3.69
$C_{28}H_{21}ON$. Calculated %: N 3.62

Action of bromotriphenylmethane on the sodium salt of carbostyril. The sodium salt of carbostyril (0.9 g) was added to a solution of bromotriphenylmethane (1.6 g) in benzene (10 ml). Heating was applied, and the reaction went very quickly. A fine precipitate, m.p. 176-180°, came down from the benzene solution. By fractional crystallization from the benzene solution obtained after the extraction of the sodium bromide, triphenylmethanol (0.45 g; well defined octahedral crystals melting at 156-160°, alone and in admixture with pure triphenylmethanol) and carbostyril (0.15 g; m.p. 198-199° after recrystallization from alcohol) were isolated.

Action of chlorotriphenylmethane on the sodium salt of carbostyril. The sodium salt of carbostyril (0.84 g) was added to a solution of chlorotriphenylmethane (1.39 g) in dry benzene (15 ml), and the mixture was heated for 30 minutes. Triphenylmethanol (0.42 g; m.p. 159-160°) and carbostyril (0.5 g; m.p. 196-198°) were isolated from the benzene solution.

Preparation of Benzylcarbostyril

Action of benzyl bromide on the silver salt of carbostyril. The silver salt of carbostyril (2.54 g) was added to a solution of benzyl bromide (1.7 g) in dry benzene (15 ml), and the mixture was heated at the boiling point of benzene for one hour. The precipitate of silver bromide was separated from the benzene solution, and the benzene was driven off. There remained a viscous, oily liquid, from which, after standing in snow, a crystalline substance (2.41 g) in the form of thick needles came down. The precipitate, after being recrystallized three times from alcohol, melted at 50-51°; the amount obtained was 1.46 g (62 %).

Found %: N 5.64

$C_{16}H_{13}NO$. Calculated %: N 5.96

Action of benzyl chloride on the silver salt of carbostyril. The silver salt of carbostyril (1.26 g) was added to a solution of benzyl chloride (0.64 g) in dry benzene (15 ml). The conditions of the reaction were similar to those in the previous experiment. A substance (0.18 g) of m.p. 50-51° was obtained from the benzene solution.

Action of benzyl bromide on the sodium salt of carbostyril. Benzyl bromide (0.93 g), dry ether (13 ml), and the sodium salt of carbostyril (0.91 g), were sealed in a tube and heated for two hours at 140-150° and for two hours at 160-170°. When the contents of the tube had cooled, they were filtered. The ether was driven off, and there remained a thick, oily, slightly yellowish liquid, which was vacuum-distilled (b.p. about 170° at 17 mm). It crystallized on standing, giving thick white needles, m.p. 95-96.5°. It had a rather unpleasant odor.

Action of benzyl chloride on the sodium salt of carbostyril. Benzyl chloride (1.8 g), dry ether (20 ml), and the sodium salt of carbostyril (2.5 g) were sealed in a tube and heated for four hours at 150-170°. When the contents of the tube had cooled, they were filtered, and from the solution, after removal of the ether, a viscous, slightly yellowish oil was obtained; it was vacuum-distilled, and it then crystallized rapidly (1.1 g, 32.7%; m.p. 95-96.5°).

Found %: N 6.08

$C_{16}H_{13}NO$. Calculated %: N 5.96

Action of benzyl bromide on the potassium salt of carbostyril. Benzyl bromide (0.71 g), dry ether (15 ml), and the potassium salt of carbostyril (1.83 g) were sealed in a tube and heated for four hours at 150-170°. The potassium bromide was separated and the ether driven off, and there remained a thick oily liquid, which crystallized in needles, m.p. 94-95° (95-96° after recrystallization from alcohol). The yield was 0.62 g (26.38%); 0.18 g of the potassium salt remained unchanged. The melting point of a mixture of this substance with benzylcarbostyril obtained by the action of benzyl chloride on the sodium salt of carbostyril was 94-95°.

Preparation of (p-Tolylmethyl)carbostyril

Action of α-bromo-p-xylene on the silver salt of carbostyril. The silver salt of carbostyril (2.4 g) was added to a solution of α-bromo-p-xylene (1.78 g) in dry benzene (15 ml), and the mixture was heated at the boiling point of benzene for one hour. The benzene was driven from the solution, and a thick, oily liquid remained. This was stood in snow, and an amorphous substance (1.1 g, 50%) of m.p. 67-72° was precipitated; the melting point after recrystallization from alcohol was 71-72°. In another experiment, in which larger amounts of starting materials were used (3.05 g of α-bromo-p-xylene and 3.92 g of the silver salt), (p-tolylmethyl)carbostyril was obtained in 94% of the theoretical yield (3.76 g).

Found %: N 5.86

$C_{17}H_{15}ON$. Calculated %: N 5.62

Action of α-bromo-p-xylene on the sodium salt of carbostyril. The sodium salt of carbostyril (0.85 g) was added to a solution of α-bromo-p-xylene (0.8 g) in dry ether (10 ml). The reaction was carried out in a sealed tube at 165-170° for two hours. The tube was opened on the next day. After evaporation of the ether, the solution yielded needlelike crystals, m.p. 106-108°. After recrystallization from alcohol the melting point rose to 131-132°. The yield was 0.8 g (73%).

Found %: N 5.92

$C_{17}H_{15}ON$. Calculated %: N 5.62

Hydrolysis Experiments

Hydrolysis of (triphenylmethyl)carbostyril. An excess of caustic potash (5 g) was added to (triphenylmethyl) carbostyril (0.2 g) contained in a small flask, and the mixture was heated for 30 minutes over a gauze. The substance did not go into solution, but formed a voluminous precipitate, which was filtered off under suction and washed until all alkali had been removed. The material obtained (0.2 g; m.p. 142-170°) was shaken with dilute hydrochloric acid, filtered, washed until neutral reaction was obtained, and extracted with ether, when a fairly considerable amount of the substance remained undissolved. The ether solution yielded a substance of m.p. 150-155°, and after further recrystallizations from ether it melted at 160-162°. The yield was 0.11 g (84.6%). In admixture with authentic triphenylmethanol it melted at 160-161°. The ether-insoluble substance was recrystallized from alcohol. The melting point after three recrystallizations was 198-199°. The yield was 0.04 g (92.0%).

TABLE

Hydrolysis of Benzylcarbostyril and of (p-Tolylmethyl)carbostyril in presence of alkali

Expt. No.	Amount of substance taken for hydrolysis	10% KOH taken (ml)	Duration and temperature of heating	Amt. obtained after neutralization with H_2SO_4, extraction with ether, and recrystallization from alcohol.
	Of benzylcarbostyrils:			
1	0.3 g of m.p. 95-96°	10	1 hr. on water bath and 1 hr. over gauze at the boil	0.26 g of m.p. 95-96°
2	0.4 g of m.p. 50-51°	10		0.3 g of m.p. 50-51°
3	0.18 g of m. p. 95-96°	4	1 hr. at 145-150°	0.15 g of m.p. 96-97°
4	0.4 g of m.p. 50-51°	6	1 hr. at 150-160°	0.33 g of m.p. 51°
	Of (p-tolylmethyl)carbostyrils:*			
5	0.24 g of m.p. 71°	10	1 hr. over gauze at the boil	0.24 g of m.p. 71°
6	0.3 g of m.p. 132°	10		0.3 g of m.p. 131-132°
7	0.3 g of m.p. 71°	4	1 hr. at 150-160°	0.3 g of m.p. 71-71.5°
8	0.24 g of m.p. 131-132°	4	1 hr. at 150-160°	0.24 g of m.p. 132°

* In every experiment the substance taken remained undissolved: it melted and settled on the bottom of the flask or tube. After the treatment, the substances were recrystallized from alcohol and yielded needlelike crystals.

Hydrolysis in presence of hydrochloric acid of the benzylcarbostyril obtained from the silver salt of carbostyril. A mixture of the benzylcarbostyril of m.p. 48.5-50° (0.5 g) and a 10% solution of hydrochloric acid (10 ml) was heated in a sealed tube for 40 minutes at 140-155° and for one hour at 155-160°. When the tube was opened, there was a strong odor of benzyl alcohol. From the aqueous solution, when cool, well formed white needles, m.p. 191°, came down (0.1 g). Apart from the crystals, some resinous material (0.39 g) was separated, and, when this was boiled with water, a further 0.06 g of carbostyril, m.p. 191-193°, was separated. Thus, the total yield of carbostyril was 0.16 g (50%). The melting point of a mixture with pure carbostyril was 196°.

Hydrolysis in presence of hydrochloric acid of the (p-tolylmethyl)carbostyril obtained from the silver salt of carbostyril. A mixture of the (p-tolylmethyl)carbostyril of m.p. 72° (0.25 g) and a 10% solution of hydrochloric acid (6 ml) was heated in a sealed tube for one hour at 130-140° and for one hour at 140-148°. From the aqueous solution, when cool, 0.05 g (30%) of carbostyril was isolated, but not all the carbostyril formed was accounted for quantitatively. A second experiment on 0.5 g of (p-tolylmethyl)carbostyril under the same conditions yielded 0.21 g (78 %) of carbostyril. In each case, when the tube was opened, there was a strong odor reminiscent of the odor of aromatic alcohols.

Hydrolysis of carbostyril methoxymethyl ether. A 10% solution of caustic potash (10 ml) was added to carbostyril methoxymethyl ether (1.28 g), and the mixture was heated at the boil for one hour. The solution was neutralized with sulfuric acid, and needlelike crystals came down. At the same time, a smell of formaldehyde was noted, and the presence of the substance in the aqueous solution was detected by a qualitative reaction. The precipitate, filtered off and washed with water, had m.p. 160-175°. It melted, after recrystallization from alcohol, at 198-199°; the yield was 0.8 g (81.5%).

Attempted hydrolysis of carbostyril ethoxymethyl ether. A mixture of the substance (0.2 g) with 10% caustic potash (10 ml) was heated in a small flask for 90 minutes. The solution was neutralized to a weakly acid reaction and extracted with ether. The extract, after evaporation of the ether, yielded 0.1 g of crystals in a fan array; they melted at 40°.

Attempted hydrolysis of carbostyril propoxymethyl ether. Expt. 1. A 0.1 N solution of caustic potash (25 ml) was added to the substance (0.7 g), and the mixture was heated under reflux in a small flask for one hour. The solution was cooled and neutralized with sulfuric acid to a weakly acid reaction. An oily substance and a small amount of white precipitate came out of the solution and were filtered off. The substance remaining on the filter (0.06 g) melted at 177-192°; it appeared to be dirty and heterogeneous. After evaporation of water from the solution, an oily substance (0.6 g) separated out, and this did not crystallize after standing for about a month. It was readily soluble in ethanol, and it separated again from its solution in ethanol, when the latter was evaporated off, as a thick yellowish oil.

Expt. 2. A 10 % solution of caustic potash (3 ml) was added to the substance to be treated (0.5 g). The mixture was heated in a sealed tube at 147-150° for one hour. When the tube was cooled, the same amount of oily liquid separated as had been taken for the hydrolysis treatment. The contents of the tube were poured into a beaker, and the solution was neutralized with 10% hydrochloric acid, when a precipitate of dirty flocculent material was formed. The solution was heated on the hotplate at the boil for 15 minutes; the precipitate did not disappear, and the oily component did not diminish in volume. The whole was then filtered, and the oil and the precipitate remained on the filter. Part of the oily material was absorbed by the filter, and a part (0.15 g) remained on the filter in the form of a cream-colored paste, which was only slightly soluble in alcohol. From the aqueous solution, after evaporation of the water, an insignificant white residue was obtained; this darkened on being heated to above 250°, and did not melt, even at 305°.

It was concluded that carbostyril propoxymethyl ether is not hydrolyzed when heated with a 10% solution of caustic potash at 150° for one hour.

Attempt to hydrolyze carbostyril propoxymethyl ether with a 10% solution of hydrochloric acid. Carbostyril propoxymethyl ether (1.45 g) and a 10% solution of hydrochloric acid, (10 ml) were heated together in a sealed tube at 140-150° for two hours. There was no excess pressure in the tube when it was opened, but an ethereal odor was noted. From the solution, when cooled, flocculent material was precipitated, and this was filtered off and washed with water. The ethereal odor of the solution gradually became less marked; finally, after the solution had stood for a long time, the odor disappeared. The flocculent precipitate was canary yellow in color. On being heated (melting point determination), it began to darken at 180° and did not melt below 240°. It was recrystallized from alcohol. Again it did not melt: at above 200° it began to darken somewhat, turning from canary yellow to beige, and at 295° a small amount of liquid appeared in the capillary, but the substance did not melt completely even at 300°. The precipitate was only partly dissolved in alcohol for the purpose of recrystallization, but the precipitate as a whole presented much the same picture as that presented by the recrystallized part.

Thus, 0.23 g of recrystallized material was obtained (it was white at first, but became canary yellow again on standing), and 0.5 g of a somewhat more grayish material remained; in the melting point test, the latter began to darken at above 230° and melted at 260-280°. This substance was insoluble in water and did not readily dissolve in alcohol. It separated from its alcoholic solution in the form of a flocculent precipitate. A Beilstein test for halogen gave a negative result. The aqueous solution was neutralized, and a qualitative test for aldehyde (ammoniacal silver nitrate solution) was made; it gave a negative result.

Isomerization Experiments

Action of benzyl bromide on benzylcarbostyril. Benzyl bromide (0.22 g) was added to benzylcarbostyril of m.p. 50-51° (0.36 g) contained in a tube having a constriction. The tube was sealed and was heated for one hour at 145-150° and for one hour at 150-160°. The tube was cooled, and it was found that the liquid had diminished somewhat in volume and had become darker in color. Excess benzyl bromide was driven off under reduced pressure, and the residual solution was cooled in snow. White crystals separated, and they were recrystallized three times from alcohol (0.15 g; m.p. 94-95°). A mixture of this substance and the substance obtained by the action of benzyl chloride on the sodium salt of carbostyril melted at 95-96°

Action of α-Bromo-p-xylene on (p-tolylmethyl) carbostyril. α-Bromo-p-xylene (0.28 g) and dry ether

(1.5 ml) were added to (p-tolylmethyl)carbostyril of m.p. 71° (0.4 g) contained in a tube having a constriction. The tube was sealed and was heated for two hours at 170-190°. The tube was cooled and opened, and the contents were poured out into a crystallizing dish. A substance that appeared to be impure and was mixed with α-bromo-p-xylene was precipitated from the ether solution. It was pressed off between small pieces of filter paper, and was recrystallized from anhydrous ethanol. The melting point after recrystallization was 128-130°. A mixture of this substance with the substance (m.p. 131°) obtained from the sodium salt of carbostyril and α-bromo-p-xylene melted at 130-131°.

Action of bromomethyl methyl ether on carbostyril methoxymethyl ether. The methoxymethyl ether of m.p. 66-67° (0.4 g) and bromomethyl methyl ether (1.2 g) were sealed in a tube having a constriction and heated for one hour at 110-120°. After being heated, the solution was darker in color. The contents of the tube were poured out into a crystallizing dish, and a substance separated which, after several washes with ether, melted at 160-190°. This substance was almost insoluble in ether and in benzene; it dissolved readily in alcohol, but did not separate out again. By recrystallization from mixed solvents – alcohol and ether – it was obtained as a white powder, which in the melting-point test began to darken at 200°, had blackened almost completely at 220°, and melted at 223-226°.

SUMMARY

1. By the action of bromomethyl methyl ether, of chloromethyl methyl ether, of bromomethyl ethyl ether, of chloromethyl ethyl ether, of bromomethyl propyl ether, and of chloromethyl propyl ether on the sodium and silver derivatives of carbostyril, the corresponding ethers were obtained:

Carbostyril methoxymethyl ether, m.p. 66-67°
Carbostyril ethoxymethyl ether, m.p. 39-40°
Carbostyril propoxymethyl ether, b.p. 192-193° at 12 mm.

2. On hydrolysis, carbostyril methoxymethyl ether gave carbostyril (in almost quantitative yield) and formaldehyde.

3. The ethoxymethyl and propoxymethyl derivatives of carbostyril do not undergo hydrolysis in dilute alkali or acid. This has been confirmed in repeated experiments. When the propoxymethyl derivative was heated with dilute acid at 140-150°, a high-melting product was obtained.

4. By the action of chlorotriphenylmethane, of benzyl bromide and chloride, and of α-bromo-p-xylene on the sodium and silver derivatives of carbostyril the following products were obtained: (triphenylmethyl) carbostyril of m.p. 180-181°; benzylcarbostyril in two forms of m.p. 50-51° and 95-96° respectively; and (p-tolylmethyl)carbostyril in two forms of m.p. 71-72° and 131-132° respectively.

5. On hydrolysis, (triphenylmethyl)carbostyril gave triphenylmethanol and carbostyril in almost quantitative yields.

6. Attempts to hydrolyze the two forms of benzylcarbostyril and the two forms of (p-tolylmethyl)carbostyril in dilute alkali did not give positive results. They were hydrolyzed in dilute acid, yielding carbostyril.

7. The sodium and potassium salts of carbostyril gave identical products when they reacted with benzyl bromide (or chloride); they gave identical products also when they reacted with bromomethyl methyl ether (or chloromethyl methyl ether).

8. An attempt to isomerize the methoxymethyl derivative of carbostyril in presence of bromomethyl methyl ether led to the formation of a high-melting product.

9. The lower-melting forms of benzylcarbostyril and (p-tolylmethyl)carbostyril were found to be isomerized when heated with the corresponding aralkyl halides into the higher-melting forms of these substances.

LITERATURE CITED

[1] A. E. Arbuzov, Bull. Acad. Sci., U.S.S.R., 211 (1939). [2] A. E. Arbuzov and M. Sh. Bastanova, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., No. 3, 459 (1952).* [3] R. Friedlander and Ostermajer, Ber. 15, 333, 335, 337 (1882); R. Friedlander and Weinberg, Ber., 15, 1421, 2103 (1882); 18, 1528 (1885). [4] R. Friedlander and F. Muller, Ber. 20, 2009 (1887).

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* See Consultants Bureau translation, p. 443.

ACTION OF ALKYL HALIDES ON SODIUM, POTASSIUM, AND SILVER DIALKYL PHOSPHOROTHIOATES

A. E. Arbuzov and O. M. Shapshinskaya

Investigation of addition reactions of "dialkylphosphorous acids" (dialkyl hydrogen phosphites or dialkyl phosphonates – Translator) has played a very important part in the study of their structure [1]. Our study of the addition of sulfur to salts of dialkylphosphorous acids, carried out in 1949-1950 [2], led us to the preparation of the corresponding metal dialkyl phosphorothioates, and we prepared sodium, potassium, and silver dialkyl phosphorothioates having ethyl, propyl, isopropyl, and butyl as alkyl radicals. Sodium, potassium, and silver dialkyl phosphorothioates are crystalline substances having definite constants.

A. E. Arbuzov and his coworkers [3,4] made a systematic study of the double-decomposition reaction between the metal derivatives of dialkylphosphorous acids and halogen derivatives of various alkanes, aranes, and organic acids. The results of these reactions varied greatly. For example, whereas the reaction between silver dialkylphosphite and chlorotriphenylmethane went according to the equation

$$(RO)_2POAg + ClC(C_6H_5)_3 = (RO)_2POC(C_6H_5)_3 + AgCl,$$

the reaction between silver dialkylphosphite and bromotriphenylmethane, on the other hand, followed the equation

$$(RO)_2POAg + BrC(C_6H_5)_3 = (RO)_2P(=O)C(C_6H_5)_3 + AgBr.$$

The reaction with the silver salt of diisopropylphosphorous acis is an exception – in this case the reaction follows the previous equation, i.e., a mixed ether being obtained. The reaction between copper salts of dialkylphosphorous acid and triphenylmethyl chloride follows the equation:

$$(RO)_2POCu + ClC(C_6H_5)_3 = (RO)_2POC(C_6H_5)_3 + CuCl.$$

The reaction between copper salts of a dialkylphosphorous acid and triphenylmethyl bromide follows the equation:

$$2(RO)_2POCu + 2BrC(C_6H_5)_3 = [(RO)_2PO]_2 + 2(C_6H_5)_3C + 2CuBr,$$

i.e., with formation of free radicals.

The reaction between chlorotriphenylmethane and the alkali salts goes according to the equation

$$(RO)_2PONa + ClC(C_6H_5)_3 = (RO)_2P(=O)C(C_6H_5)_3 + NaCl$$

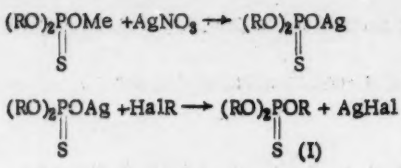
and the reaction of bromotriphenylmethane and other bromotriarylmethanes with the alkali salts (Li, K, Na, Rb, Cs) of dialkylphosphorous acids proceeds with formation of free radicals:

$$2(RO)_2POM\phi + 2BrC(C_6H_5)_3 = [(RO)_2PO]_2 + 2(C_6H_5)_3C + 2MBr.$$

Thus, it is clear that the course of the reaction between metal derivatives of dialkylphosphorous acids and halogen compounds depends on the nature of the metal, the nature of the halogen, and the structure of the organic radical. Having obtained sodium, potassium, and silver dialkyl phosphorothioates, we set ourselves the task of

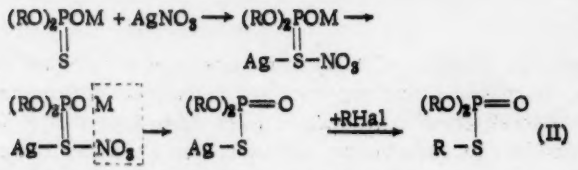
studying the effects of the nature of the metal and of the halogen in the reaction between the metal dialkyl phosphorothioates and the corresponding alkyl halides with formation of the corresponding trialkyl phosphorothioates.

When alkyl halides react with silver dialkyl phosphorothioates, the reaction of ester formation may proceed in the following directions: either to give I:



(I)

or II:



(II)

The preparation of phosphorothioic esters (I or II) could give some indication of the structure of silver dialkyl phosphorothioate, to which Pishchimuka [5] assigned the phosphorothiolate structure $(RO)_2P(=O)-SAg$.

Phosphorothioic esters both of structure I and of structure II were prepared and described by Pishchimuka. It was thus possible by comparison of the properties of phosphorothioic esters prepared by us with those described by Pishchimuka to come to a conclusion regarding their structure. In all cases we obtained ester I, which has the phosphorothionate structure $(RO)_2P(=S)OR$.

In order to study the effect of the metal of the salt on the double-decomposition reaction between metal dialkyl phosphorothioates and the corresponding alkyl halides, we have carried out reactions between sodium, potassium and silver diethyl phosphorothioates and ethyl bromide and iodide. The reactions were carried out either in a medium of dry ether or in absolute alcoholic solution. The results of the experiments are given in the table.

TABLE

No.	Reaction	Solvent	Result of reaction	B.p. (°C)	Pressure (mm Hg)	n_D^{22}	Yield (%)
1	$(C_2H_5O)_2P(=S)ONa + C_2H_5Br$	Ether	Did not go	–	–	–	–
2	$(C_2H_5O)_2P(=S)ONa + C_2H_5I$	Ether	$(C_2H_5O)_3P=S$	118	20	1.4520	2.9
3	$(C_2H_5O)_2P(=S)ONa + C_2H_5I$	Alcohol	$(C_2H_5O)_3P=S$	114	17	1.4521	3.1
4	$(C_2H_5O)_2P(=S)OK + C_2H_5Br$	Ether	Did not go	–	–	–	–
5	$(C_2H_5O)_2P(=S)OK + C_2H_5Br$	Alcohol	$(C_2H_5O)_3P=S$	118	20	1.4520	55.8
6	$(C_2H_5O)_2P(=S)OK + C_2H_5I$	Ether	$(C_2H_5O)_3P=S$	115	18	1.4523	4.2
7	$(C_2H_5O)_2P(=S)OK + C_2H_5I$	Alcohol	$(C_2H_5O)_3P=S$	111	11	1.4520	41.5
8	$(C_2H_5O)_2P(=S)OAg + C_2H_5I$	Ether	Did not go	–	–	–	–
9	$(C_2H_5O)_2P(=S)OAg + C_2H_5I$	Alcohol	$(C_2H_5O)_3P=S$	110-111	11	1.4521	33.3

The product in these experiments was always the same triethyl phosphorothioate, but the yield was dependent on the nature of the metal of the salt. Thus, the potassium and silver salts gave higher yields of ester (55.8% and 33.3%) than the sodium salt (3%).

The yield of ester is undoubtedly affected by the nature of the halogen of the alkyl halide and also by the solubility of the salt in ether or alcohol. The ester-

formation reaction goes better with ethyl iodide than with ethyl bromide. It was observed also that the formation of triethyl phosphorothioate does not go as well in ether as in alcohol. The formation of the same triethyl ester in all cases shows that sodium, potassium, and silver diethyl phosphorothioates all have the same structure.

EXPERIMENTAL

Action of Ethyl Iodide on Sodium Diethyl Phosphorothioate. Diethylphosphorous acid (25 g) was added dropwise to metallic sodium (4.1 g) in dry ether. With the first drops added, the formation of sodium diethylphosphite was evident. When addition of the acid was complete, the solution was heated until the sodium had disappeared (there was a 2.5-g excess of acid). When the solution was cool, a solution of sulfur (5 g) in benzene was added. The solution became yellow; it was boiled and left overnight. By the next day a white precipitate had settled on the bottom of the flask; the supernatent liquid was yellow. An ethereal solution of ethyl iodide (31.6 g) was added from a dropping funnel; no heating effect was observed. When the whole of the ethyl iodide had been added, the solution was heated at the boil for several hours. The precipitate at the bottom of the flask did not change in appearance; it was filtered off and washed with dry ether (37 g). The ether was distilled from the filtrate, and the residue was vacuum-distilled. At 118° under 20 mm pressure a substance (1 g, 2.9%) having n_D^{22} 1.4520 came over.

Action of Ethyl Iodide on Sodium Diethyl Phosphorothioate in Alcoholic Solution. An ethereal solution of ethyl iodide was added from a dropping funnel to a solution of sodium diethyl phosphorothioate (37 g) in absolute alcohol. There was no precipitate formed during addition of ethyl iodide. The solution was heated at the boil for three hours, and when it was cooled a small amount of white precipitate came down; it was filtered off. From the filtrate, ether and alcohol were driven off on a water bath. The residue was fractionated under reduced pressure, and a substance (1.2 g, 3.1%) of n_D^{22} 1.4521 came over at 114° under 17 mm pressure. Towards the end of the fractionation decomposition set in: white fumes appeared in the flask, and the voluminous white residue of unchanged sodium salt became distended.

Action of Ethyl Iodide on Potassium Diethyl Phosphorothioate. Metallic potassium (7 g) was introduced into dry ether contained in a round-bottomed flask provided with a reflux condenser, and an ethereal solution of diethylphosphorous acid (25 g) was added from a dropping funnel. With the first drops added white potassium diethylphosphite began to come down. When the whole of the acid had been added, the liquid was heated at the boil until the potassium had disappeared. When the solution was cool, a benzene solution of sulfur (5.79 g) was added, when the solution became yellow and a white precipitate formed on the bottom of the flask. The mixture was boiled for a long time: the white precipitate remained; the supernatent liquid was yellowish. A solution of ethyl iodide (28.2 g) in dry benzene was added to the cooled contents of the flask; there was no change in outward appearance, and no evolution of heat was to be observed. The mixture was heated at the boil for a considerable time. The residue, which had not changed in appearance, was filtered off and washed with dry ether (43 g). In the halogen test a faint flame coloration was obtained. The solvent was driven off the filtrate on a water bath, and the residue was fractionated under reduced pressure. The ester (1.5 g, 4.2%), which had n_D^{22} 1.4523, came over at 115-116° under 18 mm pressure. Towards the end of the fractionation decomposition set in.

Action of Ethyl Iodide on Potassium Diethyl Phosphorothioate in Alcoholic Solution. The 43 g of potassium salt isolated in the preceding experiment was dissolved in absolute alcohol, and to the solution obtained the ethyl iodide driven off in the course of the previous experiment was added. When the addition was almost complete, a white precipitate came down. The mixture was heated at the boil for four hours, and the amount of precipitate increased. The flask was allowed to stand overnight, and on the next day the precipitate was filtered off and washed with dry ether: 14.5 g of potassium iodide was obtained (test for halogen). When the solvent was driven from the filtrate, more potassium iodide was precipitated, and the total yield of potassium iodide was 19 g (55.4%). Addition of dry ether to the residual solution produced a white precipitate of unchanged potassium diethyl phosphorothioate (3.2 g); it gave a negative test for halogen. The residue, after removal of solvent on the water bath, was vacuum-fractionated, yielding 17 g (35.2%) of a substance of b.p. 111° at 11 mm and n_D^{22} 1.4520.

Action of Ethyl Bromide on Potassium Diethyl Phosphorothioate, in Alcoholic Solution. An excess of ethyl bromide was added to a solution of potassium diethyl phosphorothioate (3.2 g) in absolute alcohol. A white precipitate formed, and when the mixture was boiled the amount of precipitate increased; boiling was continued for four hours, and the mixture was then cooled. The precipitate (KBr: the test for halogen was positive) was filtered off. Alcohol was distilled off the filtrate, and the residue was vacuum-fractionated, yielding a substance (1.7 g, 55.8%) of b.p. 118°/20 mm and n_D^{22} 1.4520.

Action of Ethyl Iodide on Silver Diethyl Phosphorothioate. The silver salt (4.5 g) was added to dry ether contained in a round-bottomed flask fitted with a reflux condenser, and ethyl iodide (2.5 g) was added from a

dropping funnel: there was no change in outward appearance. The mixture was boiled for two hours, and the salt still did not change in appearance (the reaction had not gone). Absolute alcohol was added until the silver salt had dissolved completely, and the resulting brownish solution was heated to the boil. The whole picture changed: the solution became colorless, and a yellowish precipitate of silver iodide began to appear and continued to increase in volume as boiling continued. The mixture was cooled, and the precipitate was filtered off and washed with dry ether (3.0 g, 78.9%). Alcohol was distilled from the filtrate, and the residue was vacuum-fractionated, yielding 1 g (33.3%) of ester of b.p. 111°/14 mm and n_D^{22} 1.4520. The high yield of potassium iodide indicates that the reaction went very well, but owing to the small quantities concerned, it was difficult to make an accurate estimate of the amount of ester formed.

SUMMARY

1. The yield in the reaction leading to the formation of triethyl phosphorothioate depends on the nature of the metal in the metal dialkyl phosphonothioate, on the nature of the halogen in the alkyl halide, and on the conditions of the experiment:

a) silver and potassium diethyl phosphorothioates give the highest yields of ester;
b) the highest yields of ester are obtained in alcoholic solution.

2. In the reaction of ethyl iodide and bromide with sodium, potassium, and silver diethyl phosphorothioates the same triethyl phosphorothioate is obtained in varying yield.

LITERATURE CITED

[1] A. E. Arbuzov, "The Structure of Phosphorous Acid and its Derivatives", St. Petersburg, 1905 (Dissertation).

[2] A. E. Arbuzov and O. M. Shanshinskaya, Trans. Kazan. Chem. Tech. Inst., 16 (1949).

[3] A. E. Arbuzov, J. Russ. Phys.-Chem. Soc., 61, 231 (1929).

[4] A. E. Arbuzov et al, J. Gen. Chem., 2, 345 (1932).

[5] P. S. Pishchimuka, J. Russ. Phys.-Chem. Soc., 44, 1406 (1912).

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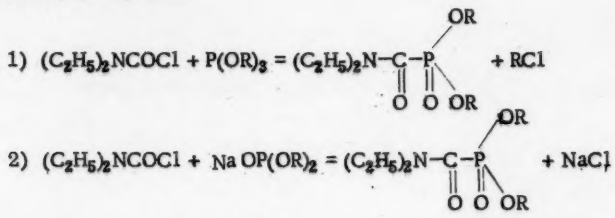
N,N-DIETHYL(DIALKOXYPHOSPHINYL)FORMAMIDES

B. A. Arbuzov and N. I. Rizpolozhensky

A. E. Arbuzov and Dunin [1] prepared ethyl diethoxyphosphinylformate by the action of chloroformic ester on triethyl phosphite, and they studied some of its properties. Nylen [2] prepared diethoxyphosphinylformamide (diethyl carbamoylphosphonate) by the action of aqueous ammonia on this ester. In 1924, Nylen [3] attempted to prepare esters of acylphosphonic (α-keto phosphonic) acids by the action of acid anhydrides on sodium diethyl phosphite. However, it was found that the reaction went in an abnormal fashion, and the expected acylphosphonic acids were not obtained. Kabachnik and Rossiiskaya [4] showed that acylphosphonic esters were obtained by the action of acid anhydrides on full esters of phosphorous acid in accordance with the A.E. Arbuzov scheme. A. E. Arbuzov and Azanovskaya [5] elucidated the source of Nylen's lack of success in his attempts to synthesize acylphosphonic esters by the action of acid anhydrides on sodium diethyl phosphite; they found that sodium diethyl phosphite may add at the carbonyl group of acylphosphonic esters.

In this paper the preparation and properties of N,N-diethyl(dialkoxyphosphinyl)formamides are described. We prepared them by the action of diethylcarbamoyl chloride both on full esters of phosphorous acid, and also on sodium dialkyl phosphites:



The two methods give approximately equal yields of N,N-diethyl(dialkoxyphosphinyl)formamides. We have prepared a number of these compounds, and their physical properties are given in the table.

We were not successful in preparing the dimethoxy compound in a pure form by either method.

EXPERIMENTAL

Attempt to Synthesize N,N-Diethyl(dimethoxyphosphinyl)formamide

Trimethyl phosphite (9.7 g) was introduced into a three-necked flask provided with reflux condenser and thermometer, and diethylcarbamoyl chloride (10.7 g) was added. There was no reaction at room temperature, and the flask was placed on the bath. At 122-125° (thermometer in the flask) methyl chloride began to be evolved. The temperature in the flask was raised gradually (over 25-30 minutes) to 135°, and was maintained at that level for 90 minutes. Evolution of methyl chloride ceased. The contents of the flask – a clear, yellowish liquid – were vacuum-distilled from an Arbuzov flask and yielded the following fractions:

Fr. I, b.p. 30- 85° at 10-11 mm Fr. II, b.p. 70-118° at 4 mm	1.5 g
Fr. III, b.p. 119-130° at 4 mm;	4 g

the residue in the flask (3 g) was a syrupy liquid.

Four vacuum fractionations were carried out without succeeding in isolating any N,N-diethyl(dimethoxyphosphinyl)formamide. Attempts to prepare this compound via sodium dimethyl phosphite were unsuccessful also.

Synthesis of N,N-Diethyl(diethoxyphosphinyl)formamide

a) A mixture of triethyl phosphite (10 g) and diethylcarbamoyl chloride (8.2 g) was heated on a bath

TABLE

No.	Formula	B.p. (°C)	Pressure (mm Hg)	d_4^{25}	n_D^{25}	MR_D Found	MR_D Calc'd
1	$(C_2H_5)_2NC(O)P(O)(OC_2H_5)_2$	117-119	4	1.0806	1.4470	58.67	58.23
2	$(C_2H_5)_2NC(O)P(O)(OC_3H_7\text{-}n)_2$	131-132	2	1.0453	1.4478	67.91	67.44
3	$(C_2H_5)_2NC(O)P(O)(OC_3H_7\text{-}i)_2$	114-115	1.5	1.0339	1.4430	68.01	67.44
4	$(C_2H_5)_2NC(O)P(O)(OC_4H_9\text{-}n)_2$	148.5-149.5	5	1.0202	1.4480	76.98	76.70
5	$(C_2H_5)_2NC(O)P(O)(OC_5H_{11}\text{-}i)_2$	155-155.5	4	0.9963	1.4482	86.54	85.95
6	$(C_2H_5)_2NC(O)P(O)(OC_6H_{13}\text{-}n)_2$	183-184.5	3.5	0.9709	1.4458	95.91	95.17

in a three-necked flask provided with reflux condenser and thermometer. At 140-145° ethyl chloride began to be evolved in appreciable amount. The reaction flask was maintained at 145-150° (thermometer in the flask) for two hours, and the temperature was then raised to 165° for 30 minutes. Separation of ethyl chloride ceased. By vacuum distillation from an Arbuzov flask the following fractions were obtained:

Fr. I, b.p. to 65° at 4 mm; 1.6 g
Fr. II, b.p. 65-115° at 4 mm; 1.2 g
Fr. III, b.p. 115-120° at 4 mm; 9 g

The residue (1 g) in the flask was a viscous yellow syrup. A second fractionation of the fraction of b.p. 115-120°/4 mm gave:

Fr. I, b.p. to 117° at 4 mm; 1.1 g
Fr. II, b.p. 117-119 at 4 mm; 7 g.

The product (7 g, 49%) had the following constants: b.p. 117-119° at 4 mm; n_D^{25} 1.4470; d_4^{25} 1.0806; yi

Found MR_D 58.67
$C_9H_{20}O_4PN$. Calculated MR_D 58.23

Found %: P 13.20; 13.27
$C_9H_{20}O_4PN$. Calculated %: P 13.12

N,N-Diethyl(diethoxyphosphinyl)formamide is a colorless odorless liquid, soluble in organic solvents such as ether, benzene, and gasoline.

b) Sodium (5 g) and gasoline of b.p. 80-120° (150 ml) were introduced into a three-necked flask provided with stirrer, reflux condenser, and dropping funnel.

Diethylphosphorous acid (21.2 g) was added from the dropping funnel, and the flask was heated for one hour on the water bath. The excess of sodium was removed, and to the cooled solution of sodium diethyl phosphite diethylcarbamoyl chloride (20.8 g) was added dropwise. Reaction was accompanied by evolution of heat. When the whole (the calculated amount) of the diethylcarbamoyl chloride had been added, the flask was heated on the water bath for 90 minutes. The precipitate of sodium chloride was separated by centrifuging, and the residual liquid after removal of the gasoline was vacuum-fractionated from an Arbuzov flask. The following fractions were isolated:

Fr. I, b.p. to 60° at 12 mm; 4 g
Fr. II, b.p. 50-109° at 3 mm; 1.8 g
Fr. III, b.p. 109-120° at 3 mm
Fr. IV, b.p. 120-125° at 3 mm } 29.2 g

Fractions III and IV were refractionated:

Fr. I, b.p. to 120° at 6 mm
Fr. II, b.p. 120-122° at 6 mm } 3 g
Fr. III, b.p. 122-123° at 6 mm; 24 g

The residue weighed 0.5 g.

The product (24 g, 65.8%) had b.p. 122-123° at 6 mm; d_4^{25} 1.0808; n_D^{25} 1.4475; yi[illegible]

Found %: P 13.19; 13.18
$C_8H_{20}O_4PN$. Calculated %: P 13.12

Synthesis of N,N-Diethyl(diisopropoxyphosphinyl)formamide

a) Triisopropyl phosphite (10.4 g) and diethylcarbamoyl chloride (6.7 g) were introduced into an Arbuzov flask. The flask was heated on an oil bath, and at 165-168° (thermometer in liquid) reaction set in with evolution of isopropyl chloride. The temperature of the bath was gradually raised over a period of 40 minutes to 185°, and separation of isopropyl chloride ceased; 3.2 g was driven over (theory requires 3.92 g). The reaction product – an almost colorless liquid – was vacuum-fractionated, yielding the following fractions:

Fr. I, b.p. to 114° at 3 mm; 1.5 g
Fr. II, b.p. 114-120° at 3 mm; 11 g.

The residue in the flask weighed 0.6 g.

Further fractionation of the fraction of b.p. 114-120°/3 mm yielded:

Fr. I, b.p. to 113° at 1 mm; 2.5 g
Fr. II, b.p. 113-114° at 1 mm; 7 g
Fr. III, b.p. 114-118° at 1 mm; 0.8 g

The product (7 g, 53.7%) – a colorless, odorless liquid – has the following constants: b.p. 113-114° at 1 mm; d_4^{25} 1.0335; n_D^{25} 1.4478; yiel[illegible]

Found %: P 11.83, 11.68
$C_{11}H_{24}O_4PN$. Calculated %: P 11.71

b) Sodium diisopropyl phosphite was prepared in a three-necked flask provided with stirrer, dropping funnel, and reflux condenser by the action of sodium (4 g, an excess) on diisopropylphosphorous acid (11.9 g). Gasoline of b.p. 80-120° served as solvent. Diethylcarbamoyl chloride (10 g) was added over 20 minutes from the dropping funnel to the sodium diisopropyl phosphite, and reaction set in with evolution of heat. When the addition was complete, the contents of the flask were boiled for 90 minutes. The precipitate of sodium chloride was removed by centrifuging [illegible], and the residue after removal of the gasoline was vacuum-fractionated from an Arbuzov flask. The following fractions were obtained:

Fr. I, b.p. to 115° at 3 mm; 2.7 g
Fr. II, b.p. 115-119° at 3 mm; 2.8 g
Fr. III, b.p. 119-120° at 3 mm; 9.4 g

The residue in the flask weighed 0.5 g.

Further fractionation of Fractions II and III yielded:

Fr. I, b.p. to 114° at 1.5 mm; 1.5 g
Fr. II, b.p. 114-115° at 1.5 mm; 10 g
Fr. III, b.p. 115.5-118° at 1.5 mm; 2 g

The product (10 g, 51.5%) had the following constants: b.p. 114-115° at 1.5 mm; d_4^{25} 1.0339; n_D^{25} 1.4430;

Found MR_D 68.01
$C_{11}H_{24}O_4PN$. Calculated MR_D 67.44

Found %: P 11.88; 11.78
$C_{11}H_{24}O_4PN$. Calculated %: P 11.71

Synthesis of N,N-Diethyl(dipropoxyphosphinyl)formamide

Sodium dipropyl phosphite was prepared in a three-necked flask provided with stirrer, reflux condenser, and dropping funnel from dipropylphosphorous acid (8.7 g) and sodium (4 g, an excess). Gasoline of b.p. 80-120°

was employed as solvent. Diethylcarbamoyl chloride (7 g) was added from the dropping funnel to the solution of sodium dipropyl phosphite, and reaction set in with evolution of heat. When the whole (the calculated amount) of the acid chloride had been added, the contents of the flask were boiled for 90 minutes. Sodium chloride, which was formed in a colloidal condition, came down as a precipitate after an addition of water (4-5 drops), and it was filtered off under suction. The residue after removal of gasoline was vacuum-fractionated from an Arbuzov flask, yielding:

Fr. I, b.p. to 130° at 2 mm; 1.8 g
Fr. II, b.p. 130-134° at 2 mm; 10.5 g

The residue weighed 0.6 g.

Further fractionation of the fraction of b.p. 130-134°/2 mm gave:

Fr. I, b.p. to 131° at 2 mm; 0.5 g
Fr. II, b.p. 131-132° at 2 mm; 7.5 g
Fr. III, b.p. 132-136° at 2 mm; 0.3 g

The product (7.5 g, 54.8%) – a colorless odorless liquid – had the following constants: b.p. 131-132° at 2 mm; d_4^{25} 1.0453; n_D^{25} 1.4478;

Found MR_D 67.91
$C_{11}H_{24}O_4PN$. Calculated MR_D 67.44

Found %: P 11.63; 11.6
$C_{11}H_{24}O_4PN$. Calculated %: P 11.71

Preparation of N,N-Diethyl(dibutoxyphosphinyl)formamide

a) Diethylcarbamoyl chloride (6.5 g) and tributyl phosphite (12 g) were introduced into an Arbuzov flask, which was heated on an oil bath. Reaction set in at 170°, butyl chloride being driven off. The temperature of the bath was raised slowly over one hour to 185°, and butyl chloride ceased to come over (4 g was driven over). The reaction product was vacuum-fractionated and yielded:

Fr. I, b.p. to 140° at 5 mm; 2.7 g
Fr. II, b.p. 140-150° at 5 mm; 9.3 g

The residue in the flask weighed 1.4 g.

Further fractionation of the fraction of b.p. 140-150° yielded:

Fr. I, b.p. to 148° at 5 mm; 1.5 g
Fr. II, b.p. 148.5-149.5 at 5 mm; 7.2 g

The product (7.2 g, 51.4%) – a colorless odorless liquid – had the following constants: b.p. 148.5-149.5° at 5 mm; d_4^{25} 1.0202; n_D^{25} 1.4480;

Found MR_D 76.98
$C_{13}H_{28}O_4PN$. Calculated MR_D 76.70

Found %: P 10.72; 10.68
$C_{13}H_{28}O_4PN$. Calculated %: P 10.57

b) Sodium dibutyl phosphite was prepared in a three-necked flask by the method described above from dibutylphosphorous acid (11.5 g) and sodium (4 g); the solvent was gasoline of b.p. 80-120°. Diethylcarbamoyl chloride (8.1 g) was added slowly to the solution of sodium dibutyl phosphite, and reaction set in with evolution of heat. When all the acid chloride had been added, the mixture was boiled on the water bath for two hours. The sodium chloride formed, which was in a colloidal condition, came out in finely crystalline form on addition of water (0.5 ml); it was filtered off under suction. The benzene was driven off under reduced pressure, and the residue was vacuum-fractionated from an Arbuzov flask, yielding:

Fr. I, b.p. to 148° at 5 mm; 2 g
Fr. II, b.p. 148-150° at 5 mm
Fr. III, b.p. 150-151° at 5 mm } 10.5 g

A further fractionation of fractions II and III yielded:

Fr. I, b.p. to 148.5° at 5 mm; 0.7 g
Fr. II, b.p. 149-150° at 5 mm; 9.4 g

The product (9.4 g, 53.7%) had the following constants: b.p. 149-150° at 5 mm; d_4^{25} 1.0205; n_D^{25} 1.4474;

Preparation of N,N-Diethyl(diisopentyloxyphosphinyl)formamide

Sodium diisopentyl phosphite was prepared by the method described above in a gasoline medium from diisopentylphosphorous acid (8.7 g) and sodium (4 g). Diethylcarbamoyl chloride (5.3 g) was added dropwise to the solution of sodium dissopentyl phosphite, and reaction set in with evolution of heat. The flask was then heated on the water bath for two hours. Sodium chloride formed in the colloidal state and was precipitated in a finely crystalline condition by addition of water (0.5 ml). The precipitate of sodium chloride was filtered off under suction, and gasoline was removed under reduced pressure. The residue was vacuum-fractionated from an Arbuzov flask:

Fr. I, b.p. to 150° at 5 mm; 2 g
Fr. II, b.p. 150-162° at 5 mm; 9 g

A further fractionation of Fraction II yielded:

Fr. I, b.p. to 155° at 4 mm; 0.5 g
Fr. II, b.p. 155-155.5° at 4 mm; 6.5 g
Fr. III, b.p. 156-160° at 4 mm; 0.4 g

The product (6.5 g, 51.8%) – a colorless, odorless liquid – had the following constants: b.p. 155-155.5° at 4 mm; d_4^{25} 0.9963; n_D^{25} 1.4482;

Found MR_D 86.54
$C_{15}H_{32}O_4PN$. Calculated MR_D 85.95

Found %: P 9.79; 9.64
$C_{15}H_{32}O_4PN$. Calculated %: P 9.66

Preparation of N,N-Diethyl(dihexyloxyphosphinyl)formamide

Sodium dihexyl phosphite was prepared in a gasoline medium from dihexylphosphorous acid (10.5 g) and sodium (4 g) by the method already described. Diethylcarbamoyl chloride (4.4 g) was added dropwise to the solution of sodium dihexyl phosphite, and reaction set in with evolution of heat. The mixture was boiled on the water bath for two hours. Sodium chloride formed in the colloidal state and was precipitated in a crystalline condition by addition of water (0.5 ml). The precipitate of sodium chloride was filtered off under suction. The residue after removal of gasoline was vacuum-fractionated from an Arbuzov flask, yielding:

Fr. I, b.p. to 168° at 2.5 mm; 1.4 g
Fr. II, b.p. 168-186° at 2.5 mm; 7.2 g

Further fractionation of Fraction II gave:

Fr. I; b.p. to 170° at 3.5 mm; 0.9 g
Fr. II, b.p. 170-183° at 3.5 mm; 0.7 g
Fr. III, b.p. 183-184.5° at 3.5 mm; 4.8 g

The product (4.8 g, 43%) – a colorless, odorless liquid – had the following constants: b.p. 183-184.5° at 3.5 mm; d_4^{25} 0.9709; n_D^{25} 1.4458;

Found MR_D 95.91
$C_{17}H_{36}O_4PN$. Calculated MR_D 95.17

Found %: P 8.96; 8.82
$C_{17}H_{36}O_4PN$. Calculated %: P 8.88

SUMMARY

By the action of diethylcarbamoyl chloride on trialkyl phosphite or on sodium dialkyl phosphite, the following new N,N-diethyl(dialkoxyphosphinyl)formamides have been prepared:

$(C_2H_5)_2N-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{P}-(OR)_2$, where R = C_2H_5; n-C_3H_7; i-C_3H_7;

n-C_4H_9; i-C_5H_{11}, and n-C_6H_{13}.

LITERATURE CITED

[1] A. E. Arbuzov and A. A. Dunin, J. Russ. Chem. Soc., 46, 295 (1914).

[2] P. Nylen , Ber. 57, 1023 (1924); 59, 1119 (1926).

[3] P. Nylen, Ber. 57, 1023 (1924).

[4] M.I. Kabachnik and P. A. Rossiiskaya, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., No. 4, 364 (1945).

[5] A.E. Arbuzov and M.M. Azanovskaya, Proc. Acad. Sci. U.S.S.R., 58, 9, 1961 (1947).

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ESTERS OF ETHYLPHOSPHONOUS ACID, AND SOME OF THEIR REACTIONS

COMMUNICATION I. FULL ESTERS OF ETHYLPHOSPHONOUS ACID

B. A. Arbuzov and N. I. Rizpolozhensky

Whereas arylphosphonous esters have received fairly detailed study [1], alkylphosphonous esters have scarcely been described. Kamai [2] has described a number of diphenyl alkylphosphonites, which he prepared by the action of diphenyl phosphorochloridite on the corresponding alkylmagnesium bromides. The cause of the lack of attention given to alkylphosphonous esters lies, evidently, in the poor accessibility of alkylphosphonous dichlorides, the starting materials for the preparation of alkylphosphonous esters.

In 1949 Kharasch [4] worked out a convenient, accessible method for the preparation of ethylphosphonous dichloride by the action of phosphorus trichloride on tetraethyl-lead, and in 1950 Fox [3] synthesized a number of alkylphosphonous dichlorides by the action of organocadmium compounds on phosphorus trichloride. From A. E. Arbuzov's work [1] it is known that arylphosphonous esters are very reactive, and this gave grounds for supposing that ethylphosphonous esters would be still more reactive.

In the present communication results are given relating to the synthesis and certain properties of esters of ethylphosphonous acid. The esters were prepared by the action of the corresponding alcohols on ethylphosphonous dichloride in presence of pyridine or triethylamine:

$$C_2H_5PCl_2 + 2ROH + 2C_5H_5N = C_2H_5P(OR)_2 + 2C_5H_5N \cdot HCl.$$

Properties of esters prepared in this way are given in Table 1.

TABLE 1

No.	Formula	B.p. (°C)	Pressure (mm Hg)	d_4^{20}	n_D^{20}	MR_D Found	MR_D Calc'd.	Yield (%)
1	$C_2H_5P(OCH_3)_2$	73.5-74.5	225	0.9516	1.4210	32.53	32.14	35.0
2	$C_2H_5P(OC_2H_5)_2$	58-60	38	0.9207	1.4212	41.34	41.39	64.5
3	$C_2H_5P(OC_3H_7\text{-}n)_2$	65-66.5	11	0.9021	1.4278	50.78	50.62	63.7
4	$C_2H_5P(OC_3H_7\text{-}i)_2$	73.5-74.5	35	0.8844	1.4169	50.64	50.62	40.0
5	$C_2H_5P(OC_4H_9\text{-}n)_2$	63-64	3	0.8977	1.4353	59.96	59.86	80.0
6	$C_2H_5P(OC_6H_{13}\text{-}n)_2$	100-101	2	0.8875	1.4435	78.41	78.33	92.0
7	$C_2H_5P(OC_8H_{17}\text{-}n)_2$	142-144	3	0.8809	1.4439	96.89	96.8	90.0
8	$C_2H_5P(OC_6H_5)_2$	115-115.5	1	1.1030	1.5650	72.57	71.13	72.5

Kamai [2] cites constants for diphenyl ethylphosphonite that differ greatly from our values: B.p. 223-225° at 11 mm; d_0^{16} 1.1923; d_D^{16} 1.5912.

Ethylphosphonous esters are colorless liquids of characteristic unpleasant odor. The odors of the methyl and the ethyl esters are very similar to those of trimethyl and triethyl phosphite respectively. They all readily oxidize in the air, oxidation being particularly vigorous in the case of the methyl and ethyl esters, which burst into flame when poured on filter paper. Hence, all operations with the esters were carried out in an atmosphere of carbon dioxide.

As was to be expected, ethylphosphonous esters were found to be extremely reactive. Being tervalent phosphorus derivatives, they react with cuprous iodide: the compound with the dimethyl ester, $C_2H_5P(OCH_3)_2 \cdot CuI$, has m.p. 160-161°; that formed with the diethyl ester, $C_2H_5P(OC_2H_5)_2 \cdot CuI$, has m.p. 167-168°. The complex compounds with the dipropyl ester, $C_2H_5P(OC_3H_7\text{-}n)_2 \cdot CuI$, and the diphenyl ester, $C_2H_5P(OC_6H_5)_2 \cdot CuI$, are noncrystallizing sirups.

Ethylphosphonous esters undergo a vigorous addition reaction with sulfur with formation of ethylphosphonothionic esters:

$$C_2H_5P(OR)_2 + S = C_2H_5\overset{\overset{S}{\|}}{P}(OR)_2.$$

The properties of the esters prepared in this way are given in Table 2.

Addition of sulfur occurs also with ethylphosphonous dichloride. As is known, this reaction has been carried out by heating ethylphosphonous dichloride with sulfur in sealed tubes [5].

TABLE 2

No.	Formula	B.p. (°C)	Pressure (mm Hg)	d_4^{20}	n_D^{20}	MR_D Found	MR_D Calc'd.	Yield (%)
1	$C_2H_5\overset{\overset{S}{\|}}{P}(OC_2H_5)_2$	80.5-81	10	1.0356	1.4558	47.84	47.82	74.0
2	$C_2H_5\overset{\overset{S}{\|}}{P}(OC_3H_7\text{-}n)_2$	69-70	1.5	1.0005	1.4622	57.08	57.80	56.5
3	$C_2H_5\overset{\overset{S}{\|}}{P}(OC_6H_5)_2$	144-144.5	1	1.1811	1.5772	77.58	78.08	65.8
4	$C_2H_5\overset{\overset{S}{\|}}{P}Cl_2$	88.5-89	46	1.3550	1.5440	36.56	37.97	71.0

We have found that in presence of a small amount of aluminum chloride the addition reaction takes place at room temperature with great vigor and with evolution of much heat. Thus, addition of 0.1 g of aluminum chloride to a mixture of ethylphosphonous dichloride (6.2 g) and sulfur (1.5 g) causes the temperature to rise to 154°.

The ethylphosphonothionic esters that we prepared are fuming liquids of characteristic odor.

By the action of halogen derivatives of hydrocarbons, ethylphosphonous esters readily undergo the A. E. Arbuzov rearrangement. To exemplify this we have carried out the following reactions: reaction of the diethyl ester with ethyl iodide and with butyl bromide, reaction of the dipropyl ester with propyl iodide, reaction of the dimethyl, diethyl, and dipropyl esters with carbon tetrachloride (Kamay [6]), and reaction of the ethyl and propyl esters with ethyl chloroacetate (A.E. Arbuzov and Dunin [7]).

TABLE 3

No.	Formula	B.p.(°C)	Pressure (mm Hg)	d_4^{20}	n_D^{20}	MR_D Found	MR_D Cal'd.	Yield %
1	$(C_2H_5)_2\overset{\overset{O}{\|}}{P}OC_2H_5$	87-88	12	0.9983	1.4353	39.27	39.13	77.0
2	$C_2H_5\overset{\overset{O}{\|}}{P}(n\text{-}C_4H_9)(OC_2H_5)$	106-108	10	0.9939	1.4382	47.09	48.36	25.7
3	$C_2H_5\overset{\overset{O}{\|}}{P}(OC_3H_7\text{-}n)(n\text{-}C_3H_7)$	104-105	8	0.9657	1.4370	48.35	48.37	30.0
4	$C_2H_5\overset{\overset{O}{\|}}{P}(CCl_3)(OCH_3)$	80-81	2.5	1.4174	1.4889	45.92	44.50	21.4
5	$C_2H_5\overset{\overset{O}{\|}}{P}(CCl_3)(OC_2H_5)$	83-84	1.5	1.3476	1.4819	50.66	49.11	22.1
6	$C_2H_5\overset{\overset{O}{\|}}{P}(CCl_3)(OC_3H_7\text{-}n)$	88-89	1.5	1.2790	1.4674	55.03	53.73	35.0
7	$C_2H_5\overset{\overset{O}{\|}}{P}(OC_2H_5)CH_2COOC_2H_5$	96-96.5	1	1.0935	1.4443	50.84	50.02	65.0
8	$C_2H_5\overset{\overset{O}{\|}}{P}(OC_3H_7\text{-}n)CH_2COOC_2H_5$	104-105	1	1.0649	1.4420	55.45	54.64	56.0

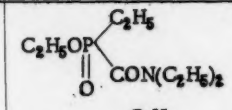
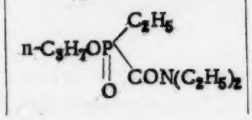
Constants of the compound are given in Table 3.

Diethylcarbamoyl chloride will react with ethylphosphonous ester, yielding the diethylamide of an alkoxy(ethyl)phosphinylformic acid according to the equation:

$$C_2H_5P(OR)_2 + (C_2H_5)_2NCOCl = C_2H_5\overset{\overset{O}{\|}}{P}(OR)CON(C_2H_5)_2 + RCl.$$

Properties of the compounds obtained are given in Table 4.

TABLE 4

No.	Formula	B.p. (°C)	Pressure (mm Hg)	d_4^{20}	n_D^{20}	MR_D Found	MR_D Cal'd.	Yield (%)
1		106-107	1.5	1.0535	1.4625	57.69	56.59	53.5
2		109-110	1	1.0341	1.4597	62.20	61.21	45.6

EXPERIMENTAL

Preparation of Ethylphosphonous Esters

1. Dimethyl ethylphosphonite. Methanol (11.9 g), triethylamine (40.5 g: an excess of 2.5 g), and ether (200 ml) were introduced into a three-necked flask provided with stirrer, reflux condenser, and dropping funnel. Ethylphosphonous dichloride of b.p. 112-114° (24.5 g) was added dropwise with snow cooling and vigorous stirring, and a stream of dry carbon dioxide was passed throughout the reaction. When the whole of the acid chloride had been added, stirring was continued for a further one hour. Triethylamine hydrochloride was filtered off, and the filtrate, after removal of ether, was vacuum-distilled. A fraction of b.p. 35-80°/213 mm was obtained, and this, after two redistillations, yielded a fraction (8 g, 30%) of b.p. 73.5-74.5°/225 mm.

Dimethyl ethylphosphonite is a colorless mobile liquid having an odor similar to that of trimethyl phosphite. It burst into flame in air, and therefore all operations from the time of its preparation to that at which the constants were determined were carried out in a carbon dioxide atmosphere. The constants found for the ester were: d_4^{20} 0.9515; n_D^{20} 1.4210; found MR_D 32.53; calculated $C_4H_{11}O_2P$ MR_D 32.14.

Analysis of ethylphosphonous esters for phosphorus by the usual methods did not give reproducible results, owing to the ready oxidizability of these substances. We carried out the analysis as follows: The weighed amount of the substance was introduced into an ampoule having very thin walls, and the capillary of the ampoule was sealed. The ampoule was placed in a thick-walled Carius tube, into which a mixture of nitric acid (2 ml; sp. gr. 1.5) and sulfuric acid (8-10 ml; sp. gr. 1.84) was poured. The tube was sealed and cooled. The tube was then shaken vigorously in order to break the ampoule, and was then heated in a furnace at 250-300° for 10-12 hours. The further course of the analysis was by Neuman's method. Very good results were obtained by the use of this modified method.

Found %: P 25.02; 24.98

$C_4H_{11}O_2P$. Calculated %: P 25.35

2. Diethyl ethylphosphonite. In the preparation of this and all succeeding esters of ethylphosphonous acid, all operations were carried out in a carbon dioxide atmosphere. Starting with ethanol (17.7 g), ethylphosphonous dichloride (25.2 g), and pyridine, (31.2 g) in a medium of ether, we obtained, after the operations described for the preparation of the dimethyl ester, diethyl ethylphosphonite (20 g, 64.3%) having the following constants: B.p. 58-60° at 38 mm; d_4^{20} 0.9275; n_D^{20} 1.4212; found MR_D 41.34; calculated $C_6H_{15}O_2P$ MR_D 41.31.

Found %: P 20.52; 20.35

$C_6H_{15}O_2P$. Calculated %: P 20.65

The ester is a colorless liquid that smells like triethyl phosphite. When poured on filter paper, it takes fire and gives forth a large amount of smoke.

3. Dipropyl ethylphosphonite. The starting materials were: propyl alcohol (30.1 g), pyridine (43 g), and ethylphosphonous dichloride (33 g). The following fractions were obtained:

Fr. I B.p. 35 - 60° at 11 mm; 4.1 g
Fr. II B.p. 60 - 65° at 11 mm; 1.2 g
Fr. III B.p. 65 - 75° at 11 mm; 34 g

Residue: 3.8 g

Further fractionation of Fractions II and III yielded dipropyl ethylphosphonite (28 g, 63.7%) having the following constants: B.p. 65-66 at 11 mm; d_4^{20}, 0.9021; n_D^{20} 1.4278; found MR_D 50.78; calculated $C_8H_{19}O_2P$ MR_D 50.62.

Found %: P 17.37; 17.36

$C_8H_{19}O_2P$. Calculated %: P 17.40

4. Diisopropyl ethylphosphonite. The starting materials were: isopropyl alcohol (20.5 g), triethylamine (30.6 g), and ethylphosphonous dichloride (22 g) in a medium of ether. Fractionation of the reaction product yielded:

Fr. I, B.p. 35 - 62° at 45 mm; 2.5 g
Fr. II, B.p. 62 - 77° at 45 mm; 2.1 g
Fr. III, B.p. 74 - 83° at 35 mm; 20.0 g

Residue: 3 g

Further fractionation of Fractions II and III yielded diisopropyl ethylphosphonite (11 g, 36%) having the following constants: B.p. 73.5-74.0° at 35 mm; d_4^{20} 0.8844; n_D^{20} 1.4169; found MR_D 50.64; calculated $C_8H_{19}O_2P$ MR_D 50.62.

Found %: P 17.58; 17.45

$C_8H_{19}O_2P$. Calculated %: P 17.40

5. Dibutyl ethylphosphonite. Starting with butyl alcohol (39.7 g), pyridine (45 g), and ethylphosphonous dichloride (35.1 g) in an ether medium, we obtained the following fractions:

Fr. I, B.p. 35 - 63° at 3 mm; 4 g
Fr. II, B.p. 63 - 80° at 3 mm; 48 g

Residue: 4.5 g

Refractionation of Fraction II yielded dibutyl ethylphosphonite (44 g, 79.4%) having the following constants: B.p. 63-63.5° at 3 mm; d_4^{20} 0.8977; n_D^{20} 1.4353; found MR_D 59.96; calculated $C_9H_{21}O_2P$ MR_D 59.86.

Found %: P 15.20; 15.16

$C_9H_{21}O_2P$. Calculated %: P 15.04

The ester is a liquid, of characteristic odor, nonwetting to glass.

6. Dihexyl ethylphosphonite. Starting with hexyl alcohol (36.2 g), pyridine (30 g), and ethylphosphonous dichloride (23.2 g) in an ether medium, we obtained the following fractions:

Fr. I, B.p. 35 - 99° at 2 mm; 0.5 g
Fr. II, B.p. 99 -102° at 2 mm; 44.5 g

Residue: 0.3 g

Refractionation yielded dihexyl ethylphosphonite (43 g, 92%) having the following constants: B.p. 100-101° at 2 mm; d_4^{20} 0.8875; n_D^{20} 1.4435; found MR_D 78.41; calculated $C_{14}H_{31}O_2P$ MR_D 78.33.

Found %: P 11.78; 11.69

$C_{14}H_{31}O_2P$. Calculated %: P 11.82

The ester is a liquid, nonwetting to glass.

7. Dioctyl ethylphosphonite. Starting with octyl alcohol (32 g), triethylamine (25 g), and ethylphosphonous dichloride (15 g), we obtained the following fractions:

Fr. I, B.p. 70 - 138° at 3 mm; 2.1 g
Fr. II, B.p. 138 - 146° at 3 mm; 31 g

Residue: 3 g

Refractionation of Fraction II yielded dioctyl ethylphosphonite (29 g, 90%) having the following constants: B.p. 142-144° at 3 mm; d_4^{20} 0.8809; n_D^{20} 1.4489; found MR_D 96.89; calculated $C_{18}H_{39}O_2P$ MR_D 96.80.

Found %: P 9.64; 9.72

$C_{18}H_{39}O_2P$. Calculated %: P 9.74

The ester does not wet glass.

8. Diphenyl ethylphosphonite. Starting with phenol (31.8 g), pyridine (23.8 g) and ethylphosphonous dichloride (22.2 g) in an ether medium, we obtained, after the usual treatment and removal of ether, a residue that gave the following fractions on being distilled:

Fr. I, B.p. to 116° at 1.5 mm; 1.5 g
Fr. II, B.p. 116 - 120° at 1.5 mm; 32 g
Fr. III, B.p. 120 - 124° at 1.5 mm; 0.3 g
Residue: 2 g

Refractionation of Fraction II yielded diphenyl ethylphosphonite (30 g, 72.5%) as a colorless liquid having the following constants: B.p. 115-115.5° at 1 mm; n_D^{20} 1.5660; d_4^{20} 1.1050; found MR_D 72.57; calculated $C_{14}H_{15}O_2P$ MR_D 71.13.

Found %: P 12.65; 12.68
$C_{14}H_{15}O_2P$. Calculated %: P 12.58

Addition of Sulfur to Ethylphosphonous Esters

1. Addition of sulfur to diethyl ethylphosphonite. Diethyl ethylphosphonite (5.7 g) and benzene (10 ml) were introduced into a 30-ml three-necked flask fitted with reflux condenser, thermometer, and tube for the passage of carbon dioxide. Finely ground sulfur (1.23 g) was added in small portions to the benzene solution. The sulfur-addition reaction proceeded with great vigor. Fractionation of the reaction product yielded:

Fr. I, B.p. 50 - 80° at 10 mm; 0.5 g
Fr. II, B.p. 80 - 82° at 10 mm; 5.2 g

Further fractionation of Fraction II yielded diethyl ethylphosphonothionate (5.1 g, 74%) having the following constants: B.p. 80.5-81.0° at 10 mm; d_4^{20} 1.0356; n_D^{20} 1.4558; found MR_D 47.82; calculated $C_6H_{15}O_2PS$ MR_D 47.84.

Found %: S 17.62; 17.50
$C_6H_{15}O_2PS$. Calculated %: S 17.57

This ester is a colorless fuming mobile liquid smelling of turpentine.

2. Addition of sulfur to diisopropyl ethylphosphonite. The materials taken for reaction were: diisopropyl ethylphosphonite (4.2 g), benzene (10 ml), and sulfur (0.76 g). Reaction was vigorous. The following fractions were obtained:

Fr. I, B.p. to 66° at 1.5 mm; 0.6 g
Fr. II, B.p. 66 - 69° at 1.5 mm; 3.6 g

Residue 0.5 g

A second fractionation yielded diisopropyl ethylphosphonothionate (2.8 g, 56.5%) as a colorless fuming liquid smelling of turpentine and having the following constants: B.p. 69-70° at 1.5 mm; d_4^{20} 1.0005; n_D^{20} 1.4622; found MR_D 57.80; calculated at $C_8H_{19}O_2PS$ MR_D 57.08.

Found %: P 14.8; 14.72; S 15.05; 15.15
$C_8H_{19}O_2PS$. Calculated %: P 14.75; S 15.2

3. Action of sulfur on diphenyl ethylphosphonite. The materials taken for reaction were diphenyl ethylphosphonite (4.3 g) and sulfur (0.6 g). The reaction, unlike that of the aliphatic esters of ethylphosphonous acid, did not go in the cold. The flask was warmed, and at 40° reaction set in. The temperature rose spontaneously to 120°, and the whole of the sulfur reacted. Distillation yielded a fraction (3.4 g, 69.5%) having the following constants: B.p. 144-145° at 1 mm; d_4^{20} 1.1811; n_D^{20} 1.5771; found MR_D 78.08; calculated $C_{14}H_{15}O_2PS$ MR_D 77.58.

Found %: S 11.36; 11.42; P 11.02; 11.18
$C_{14}H_{15}O_2PS$. Calculated %: S 11.5 P 11.12

4. Addition of sulfur to ethylphosphonous dichloride. The operations were carried out in a stream of carbon dioxide. The materials taken for reaction were ethylphosphonous dichloride (6.2 g) and sulfur (1.5 g). No reaction was observed: the sulfur dissolved when the mixture was heated to 114°, but came out again when the solution was cooled. Introduction of aluminum chloride (0.1 g) into the cold mixture of ethylphosphonous dichloride

and sulfur initiated a vigorous reaction: the temperature rose to 154°, and the liquid in the flask darkened. Distillation yielded a fraction (5.5 g, 71%) having the following constants: B.p. 88.5 - 89° 46 mm; d_4^{20} 1.3550; n_D^{20} 1.5440; found MR_D 37.97; calculated at $C_2H_5PSCl_2$ MR_D 36.56.

Found %: Cl 43.52; 43.68

$C_2H_5PSCl_2$. Calculated %: Cl 43.55

Ethylphosphonothionic dichloride is a colorless fuming liquid of characteristic odor.

Action of Cuprous Iodide on Ethylphosphonous Esters

1. Action of cuprous iodide on dimethyl ethylphosphonite. Dimethyl ethylphospphonite (1.5 g) was placed in a test tube fitted with a tube for passage of carbon dioxide, and cuprous iodide (2.3 g) was gradually added. The temperature rose to 75°, but not all of the cuprous iodide dissolved. The test tube was heated at 140-150° until the whole of the cuprous iodide had dissolved. The reaction product did not crystallize immediately. Its melting point after recrystallization from alcohol was 160-161°.

Found %: P 10.08; 9.90

$C_4H_{11}O_2P \cdot CuI$. Calculated %: P 9.93

2. Action of cuprous iodide on diethyl ethylphosphonite. Cuprous iodide (2.9 g) was added to the ester (2.3 g), and the temperature rose to 77°. The test tube was heated to 140-150°. The crystalline substance obtained melted, after being recrystallized from alcohol, at 167-168°.

Found %: P 9.17; 9.12

$C_6H_{15}O_2P \cdot CuI$. Calculated %: P 9.11

3. Action of cuprous iodide on dipropyl ethylphosphonite. When cuprous iodide (2.0 g) was added to the ester (1.9 g), the temperature rose to 50°. The test tube was heated to 140-150°, and when it was cooled a thick noncrystallizing syrup was obtained.

4. Action of cuprous iodide on diphenyl ethylphosphonite. Cuprous iodide (3.8 g) was added to diphenyl ethylphosphonite (5 g), and the temperature rose by 7°. When the mixture was heated to 150°, practically the whole of the copper salt dissolved. When it was cooled, a thick noncrystallizing syrup was obtained.

Action of Halogen Compounds on Ethylphosphonous Esters

1. Action of ethyl iodide on diethyl ethylphosphonite. The reaction, in this and in the succeeding experiments, was carried out in a stream of carbon dioxide. The ester (5.2 g) and ethyl iodide (9.5 g) were placed in the flask and heated. At 50° the contents of the flask became turbid, owing to separation of crystals, and at 104-105° reaction set in and, although further heating was not applied, the temperature in the flask rose to 140°. The liquid became clear and acquired an iodine color. Distillation yielded a fraction (4.8 g) of b.p. 84-86°/10 mm, and a second distillation gave ethyl diethylphosphinate (4.0 g, 77%) having the following constants: B.p. 87-88° at 12 mm; d_4^{20} 0.9983; n_D^{20} 1.4553; found MR_D 39.27; calculated for $C_6H_{15}O_2P$ MR_D 39.13.

Found %: P 20.57; 20.61

$C_6H_{15}O_2P$. Calculated %: P 20.65

2. Action of butyl bromide on diethyl ethylphosphonite. The reaction was carried out with 3 g of the ester and 2.8 g of butyl bromide. Separation of ethyl bromide began at 102-105°, and the temperature was finally raised to 150° and maintained at this value for 40 minutes. After three distillations, ethyl butylethylphosphinate (0.8 g) was isolated; it had the following constants: B.p. 106-108° at 10 mm; n_D^{20} 1.4382; d_4^{20} 0.9932; found MR_D 47.09; calculated for $C_8H_{19}O_2P$ MR_D 48.36.

Found %: P 17.15; 17.31

$C_8H_{19}O_2P$. Calculated %: P 17.40

3. Action of propyl iodide on dipropyl ethylphosphonite. The reaction was carried out with 3 g of the ester and 0.6 g of propyl iodide. Reaction set in at 116-118° and, although heating was discontinued, the temperature rose to 145°. The flask was then heated at 150° for 30 minutes. Two distillations yielded propyl ethylpropylphosphinate (1.09 g) having the following constants: B.p. 104-105° at 8 mm; d_4^{20} 0.9657; n_D^{20} 0.4370;) found MR_D 48.35; calculated for $C_8H_{19}O_2P$ MR_D 48.37.

Found %: P 17.19; 17.12

$C_8H_{19}O_2P$. Calculated %: P 17.40

4. Action of carbon tetrachloride on dimethyl ethylphosphonite. The ester (3.1 g) was placed in a flask, and carbon tetrachloride (4.g) was carefully added dropwise under stirring. Reaction was very vigorous, and the rate of addition was regulated so that the temperature in the flask did not exceed 50-60°. When addition was complete, the flask was heated on the water bath for 20 minutes. Fractionation yielded methyl ethyltrichloromethylphosphinate (1.3 g) having the following constants: B.p. 80-81° at 2.5 mm; d_4^{20} 1.4174; n_D^{20} 1.4889; found MR_D 45.92; calculated for $C_4H_8O_2PCl_3$ MR_D 44.50.

Found %: P 14.02; 14.00

$C_4H_8O_2PCl_3$. Calculated %: P 13.98

The ester is a colorless, mobile liquid.

5. Action of carbon tetrachloride on diethyl ethylphosphonite. Starting with the diethyl ester (4.3 g) and carbon tetrachloride (4.5 g), we obtained, after distillation, ethyl ethyltrichloromethylphosphinate (1.6 g) as a colorless liquid having b.p. 83-84° at 1.5 mm; d_4^{20} 1.3476; n_D^{20} 1.4819; found MR_D 50.66; calculated for $C_5H_{10}O_2PCl_3$ MR_D 49.11.

Found %: P 13.15; 13.0

$C_5H_{10}O_2PCl_3$. Calculated %: P 12.97

6. Action of carbon tetrachloride on dipropyl ethylphosphonite. The ester (4.0 g) and carbon tetrachloride (3.5 g) reacted very vigorously (during the reaction, the temperature was kept within the range 60-70°) and yielded propyl ethyltrichloromethylphosphinate (2.1 g) as a thick, colorless liquid having the following constants: B.p. 88-89° at 1.5 mm; d_4^{20} 1.2790; n_D^{20} 1.4674; found MR_D 55.03; calculated for $C_6H_{12}O_2PCl_3$ MR_D 53.73.

Found %: P 12.35; 12.5

$C_6H_{12}O_2PCl_3$. Calculated %: P 12.26

7. Action of ethyl chloroacetate on diethyl ethylphosphonite. Diethyl ethylphosphonite (3.7 g) and ethyl chloroacetate (4.5 g) were taken for reaction. The flask was heated on a bath, and, when the temperature in the flask was 103-104°, reaction set in and the temperature in the flask rose to 145°. The bath temperature was raised to 150° and maintained at that value for 30 minutes; separation of ethyl chloride stopped. Fractionation yielded a fraction (3.8 g) of b.p. 96-98°/1 mm, and a second fractionation yielded ethyl (ethoxycarbonylmethyl)ethylphosphinate (3.3 g, 65%) having the following constants: B.p. 96-96.5° at 1 mm; d_4^{20} 1.0935; n_D^{20} 1.4443; found MR_D 50.84; calculated for $C_8H_{17}O_4P$ MR_D 50.02.

Found %: P 15.1; 15.12

$C_8H_{17}O_4P$. Calculated %: P 14.9

This ester is a colorless liquid of pleasant odor.

8. Action of ethyl chloroacetate on dipropyl ethylphosphonite. Dipropyl ethylphosphonite (4 g) and ethyl chloroacetate (2.8 g) were taken for reaction. Reaction set in when the temperature in the flask reached 105-106°, and the temperature then rose rapidly to 145°. The flask was then heated at 150° for 30 minutes. Fractionation yielded propyl (ethoxycarbonylmethyl)ethylphosphinate having the following constants: B.p. 104-105° at 1 mm; d_4^{20} 1.0649; n_D^{20} 1.4420; found MR_D 55.45; calculated for $C_9H_{19}O_4P$ MR_D 54.64.

Found %: P 13.8; 13.75

$C_9H_{19}O_4P$. Calculated %: P 13.95

This ester is a colorless liquid of pleasant odor.

Action of Diethylcarbamoyl Chloride on Ethylphosphinous Esters

1. Action of diethylcarbamoyl chloride on diethyl ethylphosphonite. The reaction was carried out in an atmosphere of carbon dioxide. The ester (3.3 g) was heated with the acid chloride (3 g), and reaction set in at 74-76° with separation of ethyl chloride. The temperature of the bath was raised to 150° in the course of one hour and was maintained at that temperature for 40 minutes. Distillation yielded a fraction (2.6 g) of b.p. 108-111°/2.5 mm. A second distillation yielded the diethylamide of ethoxy(ethyl)phosphinylformic acid (1.8 g) having the following constants: B.p. 106-107° at 1.5 mm; d_4^{20} 1.0535; n_D^{20} 1.4625; found MR_D 56.59; calculated for $C_9H_{20}O_3PN$ MR_D 57.69.

Found %: P 13.95; 13.91

$C_9H_{20}O_3PN$. Calculated %: P 14.03

This compound is a colorless, odorless liquid.

2. Action of diethylcarbamoyl chloride on dipropyl ethylphosphonite. The ester (4.5 g) was heated with the acid chloride (3.4 g), and reaction set in at 104° and caused the temperature to rise further to 140°. The flask was heated at 140-145° for 30 minutes. Distillation yielded a fraction (3.5 g) of b.p. 110-114°/1 mm, and a second distillation yielded the diethylamide of ethyl(propoxy)phosphinylformic acid (2.7 g) having the following constants: B.p. 109-110° at 1 mm; d_4^{20} 1.0341; n_D^{20} 1.4597; found MR_D 62.20; calculated for $C_{10}H_{22}O_3PN$ MR_D 61.21.

Found %: P 13.19

$C_{10}H_{22}O_3PN$. Calculated %: P 13.19.

This ester is a colorless, mobile liquid.

SUMMARY

1. By the action of alcohols on ethylphosphonous dichloride in presence of pyridine or triethylamine we have synthesized the following esters, which have not been described previously: the dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, dihexyl, dioctyl, and diphenyl esters of ethylphosphonous acid.

2. Ethylphosphonous esters, being tervalent phosphorus derivatives, readily undergo addition reactions: they combine readily with sulfur, give complex compounds with cuprous iodide, and are very readily oxidized.

3. It has been shown that ethylphosphonous dichloride combines with sulfur in presence of aluminum chloride as catalyst.

4. A study has been made of the rearrangement of ethylphosphonous esters under the influence of alkyl halides, carbon tetrachloride, ethyl chloroacetate, and diethylcarbamoyl chloride. The reaction follows the scheme of the A. E. Arbuzov rearrangement.

5. Syntheses have been carried out for the first time of ethylphosphonothionic esters, dialkylphosphinic esters, ethyltrichloromethylphosphinic esters, (ethoxycarbonylmethyl)ethylphosphinic esters, and diethylamides of alkoxy(ethyl)phosphinylformic acids.

LITERATURE CITED

[1] A. E. Arbuzov, Dissertation, Kazan (1914); A. E. Arbuzov, J. Russ. Chem. Soc., 42, 395 (1910); A. E. Arbuzov, J. Gen. Chem., 4, 898 (1934); A.E. Arbuzov, Gilm Kamai, and O. N. Belorossova, J. Gen. Chem., 15, 766 (1945); A. E. Arbuzov and A. I. Razumov, Bull. Acad. Sci., U.S.S.R., Div. Chem. Sci., 167 (1945); Z. L. Khisamova and Gilm Kamai, J. Gen. Chem., 7, 1162 (1950). *

[2] Gilm Kamai and E. A. Gerasimova, Trans. Kazan, Chem. Tech. Inst., 15, 26 (1950).

[3] R. B. Fox., J. Am. Chem. Soc. 9, 4147 (1950).

[4] M. S. Kharasch, E. V. Jensen and S. Weinhouse, J. Am. Chem. Soc., 14, 429 (1949).

[5] F. Guichard, Ber., 32, 1572 (1899).

[6] Gilm Kamai and L. P. Egorova, J. Gen. Chem., 16, 1521 (1946); Proc. Acad. Sci. U.S.S.R. 55, 223 (1947); Gilm Kamai J. Gen. Chem., 18, 440 (1948).

[7] A. E. Arbuzov and A. A. Dunin, J. Russ. Chem. Soc., 46, 295 (1914).

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* See Consultants Bureau translation, p. 1207

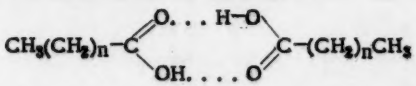
VISCOSITY-STRUCTURE RELATIONSHIP FOR PHOSPHOROUS, PHOSPHORIC, PHOSPHOROTHIONIC, AND BORIC ESTERS

B. A. Arbuzov and V. S. Vinogradova

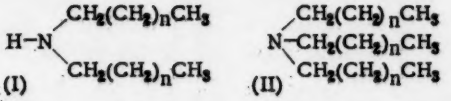
Staudinger and coworkers have found, in a series of investigations [1], that for dilute solutions of organic substances having linear molecules there is a direct relationship between viscosity and chain length. For basal molar solutions of alkanes this relationship may be expressed by the equation:

$$\eta_{sp(1.4\%)} = n \cdot y,$$

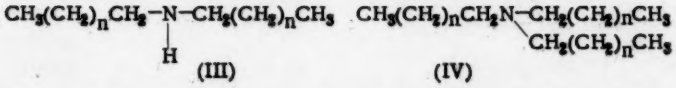
where η_{sp} is the specific viscosity, n is the number of links in the chain, and y is the specific viscosity per member of the chain for the given solvent (1.3×10^{-3} for benzene and 1.5×10^{-3} for carbon tetrachloride) [2]. By the aid of this relation Staudinger, in a number of investigations, drew inferences concerning the configurations of organic molecules in dilute solutions. Thus, Staudinger found from viscosity measurements that the higher fatty acids are present in solution in the form of extended double molecules [3]:



also [4], secondary and tertiary amines are present in solution not in the forms I and II, but in the extended forms III and IV:

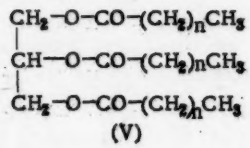


(I) (II)



(III) (IV)

Similar extended molecules were found by Staudinger also for acid anhydrides [5], esters of dibasic acids [6], and esters of glycerol (form VI, not V):



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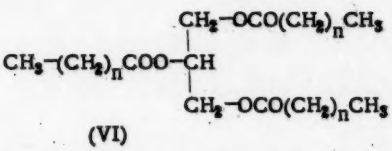
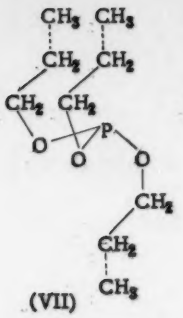


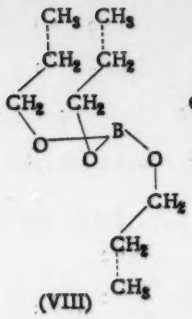
(VI)

We have found in our previous investigations [8] that the parachor can give us an idea of the way in which the chains are disposed in organic compounds of certain type. Thus, according to parachor data on phosphorous esters, only two of the three chains are disposed parallel to one another (VII) [9, 12]. A similar picture is presented by boric esters (VIII) [10] and by tertiary amines (IX) [11]: (see top of next page). However, the parachor indicates that in phosphoric esters (X) and phosphorothionic esters [12] the three chains are disposed in parallel array. It was of interest to compare the conclusions derived from these parachor data with those derived from viscosity measurements. For tertiary amines [11] parachor and viscosimetric [4] measurements gave similar results.

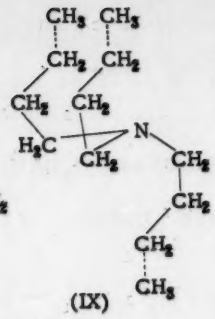
In the present communication we give results of viscosimetric measurements that we have made on phosphorous, phosphoric, phosphorothionic, and boric esters, chosen, in each case, so as to have ether chains of sufficient length. The results obtained for phosphorous esters are given in Table 1.



(VII)



(VIII)



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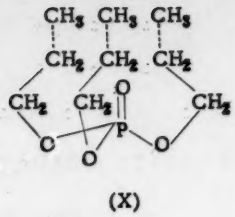


(X)

Comparison of the values of $\eta_{sp}(1.4\%)$ and Z_η found experimentally with those calculated for a parallel disposition of only two chains (–P=) and for a parallel disposition of all three chains (P≡) shows quite clearly that, according to viscosity data, in dilute solution trialkyl phosphites have only two parallel chains, which is in accord with parachor data.

The results of viscosity determinations on boric esters are summarized in Table 2.

The viscosity data for boric esters definitely indicate molecules of extended form having only two ester chains disposed in parallel fashion, which is in accord with parachor data. The results of viscosity measurements on phosphoric and phosphorothionic esters are given in Table 3.

TABLE 1

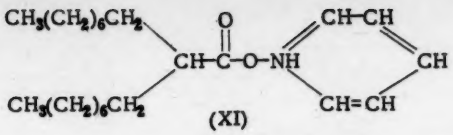
Substance	Solvent	Con. (%)	$\eta_{sp}(1.4\%)\cdot10^{-3}$ Found (at 20°)	$\eta_{sp}(1.4\%)\cdot10^{-3}$ Calcd. for –P=	$\eta_{sp}(1.4\%)\cdot10^{-3}$ Calcd. for P≡	$Z_\eta\cdot10^{-4}$* Found (at 20°)	$Z_\eta\cdot10^{-4}$* Calcd. for –P=	$Z_\eta\cdot10^{-4}$* Calcd. for P≡
Trioctyl phosphite	C_6H_6	2.85	28.4	24.7	13.0	20.3	17.7	9.3
		2.48	28.8			20.6		
		4.97	26.0			18.6		
Ditto	CCl_4	2.31	30.9	28.5	15.0	22.1	20.5	10.8
		3.19	33.0			23.5		
Trinonyl phosphite	C_6H_6	2.93	25.8	27.3	14.3	18.4	19.5	10.2
		3.64	23.9			17.0		
Ditto	CCl_4	2.77	28.3	31.5	16.5	20.2	22.7	11.9
		3.91	31.3			22.3		
Tridecyl phosphite	C_6H_6	2.88	29.8	29.9	15.6	21.3	21.4	11.6
		3.69	26.3			18.8		
Ditto	CCl_4	2.76	37.4	34.5	18.0	26.8	24.8	13.0
		3.32	40.3			28.8		
Trihexadecyl phosphite	C_6H_6	3.8	40.6	45.5	23.4	29.0	32.5	16.7
Ditto	CCl_4	3.5	51.6	52.5	27.0	36.8	37.8	19.4

* $Z\eta$ is calculated not for basal molar solutions, but for a solution having a concentration in g/liter of Kequiv. (which is $0.93\cdot10^{-4}$ for benzene and $1.08\cdot10^{-4}$ for carbon tetrachloride.

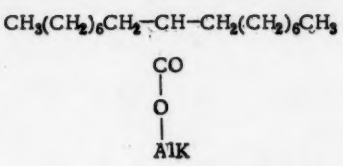
As the results in Table 3 show, the values of η_{sp} (1.4%) and Z_η indicate an extended form of molecule for phosphoric and phosphorothionic esters in dilute solution and are thus at variance with parachor data for these compounds, according to which all the three esters interact with one another. The nonaccord of these conclusions concerning the structures of phosphoric and phosphorothionic esters makes it desirable to carry out further investigation into the questions: In the analysis of parachor data, what do the corrections for parallelism indicate? What does viscosity measurement yield for molecules of branched structure?

The results of numerous researches by Staudinger and coworkers indicate that, according to viscosity data, molecules have an extended form in solutions. The results of Staudinger [13] according to which the pyridine salt of dioctylacetic acid has the structure XI, which has a nonextended form and not the extended form of a dioctylacetic ester (XII), are not very convincing, for the chains have in each case the same length (17 members*):

* If all the atoms of the pyridine ring are considered to be in the chain.



(XI)



(XII)

TABLE 2

Substance	Solvent	Concen. %	$\eta_{sp}(1.4\%)\cdot10^{-3}$			$Z_\eta\cdot10^{-4}$		
			Found at 20°	Calcd. for		Found at 20°	Calcd. for	
				–B=	B≡		–B=	B≡
Triheptyl borate	C_6H_6	2.86 4.63	23.2 26.3	22.1	11.7	16.6 18.8	15.8	8.4
Ditto	CCl_4	2.96 2.77	22.6 22.8	25.5	13.5	16.2 16.3	18.4	9.7
Trioctyl borate	C_6H_6	4.25	26.9	24.7	13.0	19.8	17.7	9.3
Ditto	CCl_4	3.92 5.56	25.6 28.1	28.5	15.0	18.3 20.0	20.5	10.8
Trinonyl borate	C_6H_6	2.36 2.95	28.5 26.3	27.3	14.3	20.4 18.8	19.5	10.2
Ditto	CCl_4	2.44 3.72	36.4 33.3	31.5	16.5	26.0 23.8	22.7	11.9
Tridecyl borate	C_6H_6	3.60	29.2	29.9	15.6	20.8	21.4	11.2
Ditto	CCl_4	2.22 2.22 3.15	37.9 38.7 38.8	34.5	18.0	27.1 27.6 27.7	24.8	13.0
Tricyclohexyl borate	C_6H_6	3.07 4.17	22.3 19.0	19.6* 19.6	7.4 7.4	15.9 13.6	14.0* 14.0	8.6 8.6
Trihexadecyl borate	C_6H_6	4.89	49.0	45.5	23.4	35.0	32.6	16.7
Ditto	CCl_4	3.68	50.8	52.5	27.7	36.3	37.8	19.5

* The cyclohexyl radical being considered to provide six members of the chain.

Thus, viscosity data give an indication of the length of the longest chain of atoms in the molecule, and it is possible that they do not form an adequate criterion of the disposition of individual chains in the molecule.

From this point of view viscosity measurements on cyclic compounds having a large number of atoms in the ring are of interest. Staudinger and Bauer [14] have published results on the viscosities of large-ring compounds synthesized by Ruzicka.

If it is considered that the viscosity gives the length of the molecule, then for a large ring it should

TABLE 3

Substance	Solvent	Concentration, %	η_{sp} (1.4%)·10^{-3}			$Z\eta \cdot 10^{-4}$		
			Found at 20°	Calcd. for		Found at 20°	Calcd. for	
				−P=	P≡		−P=	P≡
Trihexyl phosphate	C_6H_6	3.38	23.8	19.5	11.7	17.0	14.0	8.4
		3.47	18.8			13.4		
Ditto	CCl_4	3.51	19.12	22.5	13.5	13.7	16.2	9.7
Trioctyl phosphate	C_6H_6	1.57	26.9	24.7	14.3	19.2	17.7	10.2
		2.53	25.2			18.0		
		3.74	28.5			20.4		
Ditto	CCl_4	3.09	26.7	28.5	16.5	19.1	20.5	11.9
		4.51	27.1			19.3		
Trihexyl phosphorothionate	C_6H_6	3.69	21.3	19.5	11.7	15.2	14.0	8.4
		4.56	21.3			15.2		
Ditto	CCl_4	3.40	25.2	22.5	13.5	18.0	16.2	9.7
		2.24	27.1			19.3		
Trioctyl phosphorothionate	C_6H_6	3.83	27.0	24.7	14.3	19.8	17.7	10.2

correspond to half of the number of members in the ring. Staudinger's results [15] for carbon tetrachloride solutions of large-ring compounds are given in Table 4.

TABLE 4

Substance	No. of members in ring (n)	No. of members in chain of length ∼ n/2	$Z\eta \cdot 10^{-4}$			
			Found	Calcd. for n	Calcd. for ∼ n/2	Calcd. for n/2
Cyclopentadecane	15	8	12.0	16.2	8.7	8.6
Methylcyclopentadecane	15	9	14.0	16.2	9.8	8.6
Cyclotriacontane	30	16	30.0	32.4	17.3	16.2
Cyclotriacontanone*	30	17	29.9	32.4	18.4	17.3
1,16-Cyclotriacontanedione	30	18	31.5	32.4	19.4	17.3
1,16-Dimethylcyclotriacontane	30	18	29.1	32.4	19.4	17.3
Cyclotetratriacontane	34	18	32.2	36.8	19.4	18.3
Cyclotetratriacontanone	34	19	31.4	36.8	20.5	19.4

* A methyl side chain or a carbonyl group lengthen the chain by unity.

In the column headed "$Z_\eta \cdot 10^{-4}$ calcd. for ∼n/2" Staudinger gives values of Z_η for paraffins having chains of approximately n/2 members. In the last column we have given values of Z_η calculated for n/2*. In the first paper [14] Staudinger regards the difference between the value of η_{sp} found for these large-ring compounds and that calculated for n/2 as the ring increment, and he points out that it is impossible to say from the results obtained whether there is a simple relation between the value of the ring increment and the number of members of the ring.

In the later article [15], from which Table 4 is taken, Staudinger does not refer to the ring increment, but explains the large discrepancy (between the value of Z_η calculated for n/2 and the value of Z_η found) on the hypothesis that the parallel arrangement of the two halves of the ring renders them more rigid: they therefore

* Treating methyl and carbonyl each as one member of the chain.

TABLE 5

Substance	Solvent	No. of members (n)	Concen. %	η_{sp} (1.4%)·10^{-3}		$Z_\eta \cdot 10^{-4}$	
				Found at 20°	Calcd. for n	Found	Calcd. for n
Triethylene glycol ester of succinic acid	C_6H_6	14	3.46	32.6	18.2	23.3	13.1
		14	5.14	32.0	18.2	22.9	13.1
		14	3.22	29.9	18.2	20.7	13.1
Ditto	CCl_4	14	3.33	33.8	21.0	24.1	15.1
		14	5.19	33.3	21.0	23.8	15.1
1,3-Propanediol ester of sebacic acid	C_6H_6	15	2.42	29.3	19.5	21.0	13.9
		15	5.72	26.6	19.5	18.7	13.9
Ditto	CCl_4	15	3.76	30.7	22.5	21.9	16.2
		15	3.71	29.7	22.5	21.2	16.2
Triethylene glycol ester of adipic acid	C_6H_6	16	2.43	28.2	20.8	20.1	14.9
		16	4.30	31.7	20.8	22.7	14.9
		16	5.75	30.1	20.8	21.5	14.9
Ditto	CCl_4	16	4.55	36.2	24.0	25.8	17.3
		16	5.00	36.1	24.0	25.7	17.3
Diethylene glycol ester of sebacic acid	C_6H_6	17	3.72	31.8	22.1	23.3	15.8
Triethylene glycol ester of sebacic acid	C_6H_6	20	4.19	30.1	26.0	21.5	18.6
		20	6.14	31.7	26.0	22.7	18.6
Ditto	CCl_4	20	2.70	39.6	30.0	28.3	21.6
		20	3.46	40.2	30.0	28.7	21.6

shorten to a less extent than the paraffins having n/2 chain members, i.e., they have a greater viscosimetric length than paraffin molecules having n/2 members. Also, a comparison of the values given in Table 4 of $Z\eta$ found and $Z\eta$ calculated for n members in the ring indicates that these data are fairly close together, and it is quite possible that in this case also the viscosity indicates the longest chain of atoms in the molecule, all the atoms forming part of the chain being counted.

In order to extend the data available on the viscosity of large-ring compounds, we have prepared cyclic esters having a large number of members in the ring, and we have measured their viscosities. It must be remarked, however, that in this case we have not succeeded in obtaining results that are in good agreement; an increase in accuracy is called for. Results of measurements in carbon tetrachloride are given in Table 5.

The results in Table 5 show that the experimental values for the viscosities of large-ring esters are considerably higher than those calculated for the total number of members in the ring. There is no explanation for this at present.

It should be noted that a similar exaltation of the experimental viscosity values in comparison with the calculated values was observed by Staudinger in the case of substituted amides of higher fatty acids [16]; in chloroform solvent the exaltation was 14 units. This exaltation was ascribed by Staudinger to the effect of the amide group.

EXPERIMENTAL

The specific viscosity of the compounds investigated was determined from the usual formula:

$$\eta_{sp} = \frac{t_2 \cdot d_2}{t_1 \cdot d_1} - 1,$$

where t_1, d_1 and t_2, d_2 are the times of flow and the densities for the pure solvent and for the solution. The viscosity measurements were carried out in an open viscometer similar to that used by Staudinger [17]. The volumes of the bulbs of the viscometer were 1 and 10 ml respectively, the diameter of the capillary was 0.18 mm,

and its length was 95 mm. Cryoscopic benzene, freshly distilled over sodium, and carbon tetrachloride were chosen as solvents; their times of flow in our viscometer were about 300 and 250 seconds respectively.

The measurements were carried out in a thermostat at 20° (±0.1°). A solution of volume 10 ml and concentration not exceeding 3-5 wt.-% was prepared. The lower limit of concentration was chosen so that the difference in the times of flow of the solution and of the pure solvent should not be less than ten seconds. By means of a pipet, 3 ml of the solution was introduced through a sintered glass filter into the lower bulb. The time of flow was measured to the nearest 0.1 sec, the measurement being repeated five or six times and the mean value determined. The divergence in the readings did not exceed 0.2-0.4 sec. The air that entered the apparatus as liquid flowed out was dried over phosphoric anhydride in a five-liter bottle.

The phosphorous esters, prepared by transesterification of triethyl phosphite with the corresponding alcohols, were:

1. Trioctyl phosphite: b.p. 212-214°/2 mm; n_D^{20} 1.4475; d_4^{20} 0.8907 [12].
2. Trinonyl phosphite: b.p. 226.5-227.5°/1 mm; n_D^{20} 1.4495; d_0^{20} 0.8879 [12].
3. Tridecyl phosphite: b.p. 236.5-237.5/1.5 mm; n_D^{20} 1.4518; d_0^{20} 0.8842 [12].
4. Trihexadecyl phosphite: b.p. 288-290°/0.4 mm, m.p. 51° [18].

The boric esters, prepared, apart from No. 8 and No. 9, by reaction of the corresponding alcohol with boric acid, were:

5. Triheptyl borate: b.p. 185-186°/2 mm; n_D^{20} 1.4280; d_4^{20} 0.8398 [8].
6. Trioctyl borate: b.p. 200-201°/2 mm; n_D^{20} 1.4360; d_4^{20} 0.8548 [8].
7. Tridecyl borate: b.p. 274-276°/0.5 mm; n_D^{20} 1.4440; d_4^{20} 0.8581 [8].
8. Tricyclohexyl borate, prepared by transesterification of butyl borate: b.p. 153-155°/2 mm; d_0^{40} 0.9567 [8].
9. Trinonyl borate, prepared for the first time by heating boric acid (1 g) with nonyl alcohol (b.p. 92-94°/8 mm) (8 g) and then driving off water under vacuum. After two redistillations: b.p. 228-230°/1.5 mm; n_D^{20} 1.4405; d_4^{20} 0.8575.

Found %: B 2.25
$C_{27}H_{57}O_3B$. Calculated %: B 2.34

10. Trihexadecyl borate: b.p. 328-329°/<0.5 mm; m.p. 43-44° [18].

The phosphoric esters, prepared by the action of phosphoryl chloride on the corresponding alcohols in presence of pyridine [19], were:

11. Trihexyl phosphate: b.p. 187-188°/2 mm; n_D^{20} 1.4340; d_0^{20} 0.9396 [12].
12. Trioctyl phosphate: b.p. 225-227°/2 mm; n_D^{20} 1.4410; d_0^{20} 0.9200 [12].

The phosphorothionic esters, prepared by addition of sulfur to the corresponding phosphite, were:

13. Trihexyl phosphorothionate: b.p. 188-188.5/2.5 mm; n_D^{20} 1.4568; d_0^{20} 0.9501 [12].
14. Trioctyl phosphorothionate: b.p. 224-226°/<0.5 mm; n_D^{20} 1.4592; d_0^{20} 0.9293 [12].

The remaining esters were:

15. Trimethylene sebacate: b.p. 145-147°/4 mm; n_D^{20} 1.4700; d_0^{60} 1.0405 [20].
16. Diethylene glycol ester of sebacic acid: b.p. 175-178°/3.5-4 mm; d_0^{60} 1.0650 [8,20].
17, 18, and 19. Cyclic esters of dibasic acids, the preparations of which are given below.

Preparation of the cyclic ester of triethylene glycol with adipic acid. Adipic acid (30 g) and triethylene glycol (b.p. 149-150°/4 mm) (33 g) were heated together for two hours at a bath temperature of 220° in a small flask having an outlet tube. Some water separated, and heating was then continued at a bath temperature of 220-230° under reduced pressure (15 mm for one hour and then 5 mm for 30 minutes). The polyester obtained formed a thick dark mass. It was depolymerized by Carothers' method [20], which was modified by the use of an aluminum block in which a hole had been drilled to carry the reaction vessel (diameter of block 14 cm, height 17 cm; diameter of hole 7 cm, depth 15 cm); the block was provided with a nichrome-wire winding for heating purposes and was lagged with asbestos. The modification permitted the more ready maintenance of a constant high temperature. Depolymerization was carried out in a cylindrical glass vessel having a narrow neck and a fused-on delivery tube. The vessel was placed in the hole in the block, and the space between the vessel

and the wall of the hole was packed with fine copper filings, in which a thermometer was placed. With such an aluminum block it was found possible by the aid of a rheostat to maintain a temperature constant to 1-2° in the range 250-300°. This arrangement is safe in use and enables the desired temperature to be maintained without the use of selected liquids of the required boiling point, as described by Carothers.

The polyester from triethylene glycol and adipic acid was placed in the depolymerization vessel, and the catalyst ($SnCl_2 \cdot 2H_2O$, 0.5 g) was added. Depolymerization was carried out at a block temperature of 250-270° and under a pressure of 3-4 mm. Depolymerization was rapid: 40 g of distillate was obtained in 3 hrs 30 min. Redistillation of the distillate gave a fraction (23 g) of b.p. 192-195°/5 mm which rapidly crystallized. After a further redistillation the fraction boiled at 172-174°/2.5 mm and yielded a slightly yellowish liquid, which crystallized immediately. The cyclic ester has a powerful, persistent, tarry odor.

Found: M 260
$C_{12}H_{20}O_6$. Calculated: M 260 (Rast's method)

Found %: C 55.59; H 7.54
$C_{12}H_{20}O_6$. Calculated %: C 55.38; H 7.74

Preparation of the cyclic ester of triethylene glycol with succinic acid. Succinic acid (23.5 g) and triethylene glycol (33 g) were heated together for two hours at a bath temperature of 200-210°, for one hour under 12 mm at 220°, and then for 30 minutes under 2 mm at 225°. The polyester formed was a thick, immobile mass. Depolymerization was carried out in the previously described apparatus; the catalyst was $SnCl_2 \cdot 2H_2O$ (0.5 g) and the block temperature was 272-275°. The reaction was complete in 3 hrs 30 min; the pressure at the beginning of the depolymerization was 2.5 mm, but rose towards the end to 6 mm. The distillate (46 g) was a golden-yellow liquid.

Fractionation gave:

Fraction 1, b.p. 110-163°/3 mm - 10 g.
Fraction 2, b.p. 163-168°/3 mm - 33 g.

A second fractionation of Fraction 2 gave a product of b.p. 169-170°/3 mm (28 g); it was a thick yellowish liquid having a tarry odor. On the next day it had crystallized (m.p. 54-55°). The melting point after recrystallization from methanol was 57-58°.

Found: M 254
$C_{10}H_{16}O_6$. Calculated: M 232 (Rast's method)

Found %: C 51.49; H 6.80
$C_{10}H_{16}O_6$. Calculated %: C 51.71; H 6.94

Preparation of the cyclic ester of triethylene glycol with sebacic acid. Sebacic acid (10 g) and triethylene glycol (8.0 g) were heated together for two hours at 210-220°, for one hour at 220° under 15 mm pressure, and then for 30 minutes at 220-230° under 3 mm. Depolymerization was carried out in presence of $SnCl_2 \cdot 2H_2O$ at 265-270° under 3 mm pressure. Depolymerization was slow (one drop per minute, and towards the end, one gram per hour), and the total distillate was 12 g. Fractionation gave a fraction of b.p. 202-204° (uncorr.)/3 mm (3 g). It was a thick liquid; when it was rubbed out on the hand there was a persistent, unpleasant odor, reminiscent of musk.

Found %: C 60.61; H 8.74
$C_{16}H_{28}O_6$. Calculated %: C 60.79; H 8.93

SUMMARY

1. The specific viscosities have been determined of dilute solutions in benzene and in carbon tetrachloride of phosphorous and boric esters having long hydrocarbon radicals (from octyl to decyl). Comparison of the values found for η_{sp} (1.4%) and $Z\eta$ with those calculated indicates that the molecules of these esters are in the extended form in dilute solution, which is in agreement with parachor data.

2. The specific viscosities have been determined of dilute solutions in benzene and in carbon tetrachloride of phosphoric and phosphorothionic esters having hexyl and octyl radicals. Comparison of the values found for η_{sp} (1.4%) and $Z\eta$ with those calculated indicates that the molecules of phosphoric and phosphorothionic esters are in the extended form in dilute solution, which is not in agreement with conclusions based on a study of the parachors of these esters.

3. When a comparison is made of the found and calculated values of η_{sp} (1.4%) and $Z\eta$ for macrocyclic compounds having rings of 15-34 members for which viscosity data are available in the literature, it is found that the viscosity values found are closer to those calculated for the total number of members in the ring than to those calculated, following Staudinger's views, for a half of that number.

4. Cyclic esters of triethylene glycol with succinic, adipic, and sebacic acids have been synthesized, and viscosity measurements have been made on their dilute solutions. The values found for η_{sp} (1.4%) and $Z\eta$ are greater than those calculated for the total number of members in the ring.

5. Our results show that further investigation is required into the question of what measurements of viscosity tell us concerning molecules of branched structure and molecules having branched rings, and they show that further investigation is required also into the nature of Gibling's corrections for parallelism in the determination of molecular structure by the parachor method.

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LITERATURE CITED

[1] H. Staudinger, "Macromolecular Organic Compounds. Rubber and Cellulose", United Sci. Tech. Press, 1935, p. 57; H. Staudinger and F. Staiger, Ber. 68, 707 (1935); H. Staudinger and H. Schwalenstocker, ibid. 727; H Staudinger and A. Steinhoper, ibid, 471, Ann. 517,56 (1935).

[2] H. Staudinger and H. Schwalenstocker, Ber. 68, 728 (1935).

[3] H. Staudinger and E. Ochiai, Z. phys. Chem. 158, 45 (1932).

[4] H. Staudinger and K. Rossler, Ber. 69, 52 (1936).

[5] H. Staudinger and H. Schwalenstocker, Ber. 68, 727 (1935).

[6] Ibid, p. 742.

[7] Ibid, p. 746.

[8] V. Vinogradova, Sci. Mem. Kazan Univ. 110, Book 9, (1950).

[9] B. A. Arbuzov and V. S. Vinogradova, Ibid., p. 21.

[10] B. A. Arbuzov and V. S. Vinogradova, Proc. Acad. Sci. USSR, 55, 415 (1947).

[11] B. A. Arbuzov and L. M. Guzhavina, Proc. Acad. Sci. USSR, 61, 63 (1948).

[12] B. A. Arbuzov and V. S. Vinogradova, Bull. Acad. Sci. USSR Div. Chem. Sci. 733 (1951).

[13] H. Staudinger, "Macromolecular Organic Compounds", United Sci. Tech. Press, 1935, p. 78

[14] H. Staudinger and R. C. Bauer, Helv. Chim. Acta 17, 863 (1934).

[15] H. Staudinger, Makromol. Chem. 4, 289 (1950).

[16] H. Staudinger and Rossler, Ber. 69, 63 (1936).

[17] H. Staudinger and Steiger, Ber. 68, 707 (1935).

[18] B. A. Arbuzov and V. S. Vinogradova, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 3, 505 (1952).*

[19] T. Milobendzky, A. Sachnowsky, Ch. Polsky, 15, 34 (1917).

[20] W. Carothers, J. Am. Chem. Soc. 57, 931 (1935).

* See Consultants Bureau translation, p. 483.

DIPOLE MOMENTS OF N,N-DIETHYL(DIALKOXYPHOSPHINYL)FORMAMIDES

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N,N-Diethyl(dialkoxyphosphinyl)formamides form an interesting group of quinquevalent phosphorus derivatives containing adjoining P=O and O=C–NR_2 groups. There are no available data on the dipole moments of these substances, and we considered that it would be of interest to determine these properties.

The disposition of the individual bond moments in N,N-diethyl(dialkoxyphosphinyl)formamides is similar to that found in phosphoric esters. This circumstance makes it possible for us to discuss a number of possible structures for N,N-diethyl(dialkoxyphosphinyl)formamides, the spatial arrangement of individual groups, and the possibility of the movement of certain groups around the appropriate bonds as axes. We have measured the dipole moments of six N,N-diethyl(dialkoxyphosphinyl)formamides [1], and have obtained the results given in Table 1.

TABLE 1

No.	Substance	Dipole moment (D)
1	$(C_2H_5O)_2$–P(=O)–C(=O)–$N(C_2H_5)_2$	2.91
2	$(n\text{-}C_3H_7O)_2$–P(=O)–C(=O)–$N(C_2H_5)_2$	3.02
3	$(i\text{-}C_3H_7O)_2$–P(=O)–C(=O)–$N(C_2H_5)_2$	2.88
4	$(n\text{-}C_4H_9O)_2$–P(=O)–C(=O)–$N(C_2H_5)_2$	3.09
5	$(i\text{-}C_5H_{11}O)_2$–P(=O)–C(=O)–$N(C_2H_5)_2$	2.92
6	$(C_6H_{13}O)_2$–P(=O)–C(=O)–$N(C_2H_5)_2$	2.94

From the results given in Table 1 it will be seen that the dipole moments of N,N-diethyl(dialkoxyphosphinyl)formamides vary from 2.88 D to 3.09 D, the mean value for the homologous series being 2.96 D, which is practically the same as the mean value of the dipole moments of phosphoric esters, O=P–$(OR)_3$, which is 3.08 D for the homologous series [2].

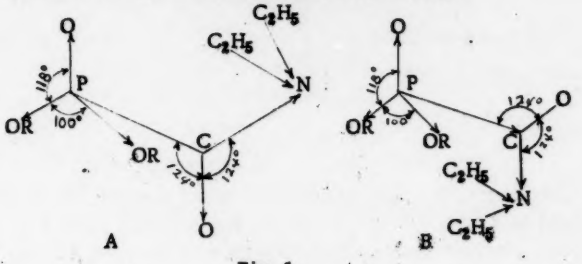

Fig. 1

The molecule of an N,N-diethyl(dialkoxyphosphinyl)formamide may be represented by the following two configurations (A and B in Fig. 1, which represent two possible arrangements of the group –C(=O)–NR with respect to the bond P–C.

In the construction of molecular configurations for an N,N-diethyl(dialkoxyphosphinyl)formamide, the valency angles in O=C–P and O=C–N are taken as 124°, this assumption being based on the constant valency angle of approximately 124° that is observed for the group O=C–X in studies by the electronographic method of valency angles in various compounds containing doubly bound carbon.

We assume the configuration of the diethylamido group to be similar to that of trimethylamine, which has been established by electronographic methods [3]: the nitrogen valency angle is taken as 108°.

The dipole moment of the N,N-diethyl(dialkoxyphosphinyl)formamide molecule calculated by the Smyth-Lewis formula [4], free rotation being assumed for the group OR around the bond P–O at an angle of 70° and for the groups –C(=O)–$N(C_2H_5)_2$ around P–C, is 3.33 D.

The dipole moment of the P=O bond is assumed to be 3.5 D, the value 1.2 D is assumed for P–O, 1.12 D is assumed for O–R, 0.9 D for P–C, 2.3 D for C=O and 0.8 D for the group –C(=O)–$N(C_2H_5)_2$ [3]. The angle O=P–O is

assumed to be 118°, the angle O–P–O to be 100°, and the oxygen angle to be 110°, as in phosphoric esters [8].

Thus, the dipole moment of this molecule calculated on the assumption of free rotation of the irregular groups OR and $-\overset{\overset{O}{\|}}{C}-N(C_2H_5)_2$, exceeds the experimentally found value by only 0.37 D.

However, the agreement between the value of the dipole moment calculated for completely free rotation and that found experimentally does not altogether prove the presence of free rotation. Thus, the calculations we have made for orthocarbonic, orthosilicic, orthotitanic, phosphorous, and phosphoric esters of interatomic distances of individual groups on the assumption of free rotation, taking into account the radius of action of Van der Waals forces due to methyl and methylene groups, show that for these esters it is doubtful whether free rotation of the irregular groups is possible, for there is a great measure of superposition of Van der Waals spheres of action associated with methyl or methylene groups of adjacent alkoxy chains [5].

For N,N-diethyl(dialkoxyphosphinyl)formamides the configurations C and D (Fig.2) show the greatest overlap in the Van der Waals spheres of influence associated with alkoxy groups and are therefore of low probability for any position of the group $-\overset{\overset{O}{\|}}{C}-N(C_2H_5)_2$. The calculated dipole moments for the configurations C and D are 5.36 D and 1.76 D respectively.

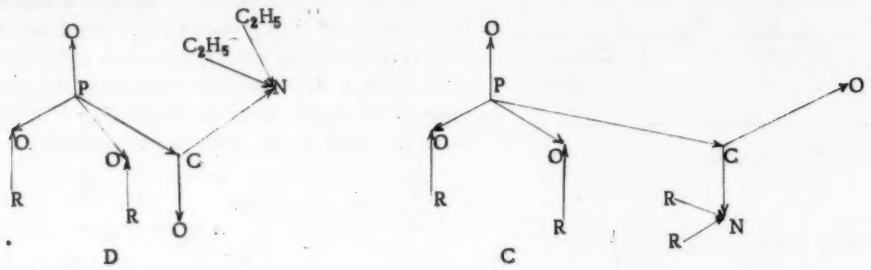

Fig. 2

Configurations of the molecule in which the OR groups are arranged in a plane perpendicular to the paper and to the bond P==O (A_1 and B_1, Fig.3) do not show overlap overlap of Van der Waals spheres of action. The dipole-moment values are 4.00 D for configuration A_1, and 2.09 D for configuration B_1. Configurations A_2 and B_2 (Fig.4) also do not show overlap of Van der Waals spheres of action, and the respective dipole-moment values are 3.46 D and 2.53 D.

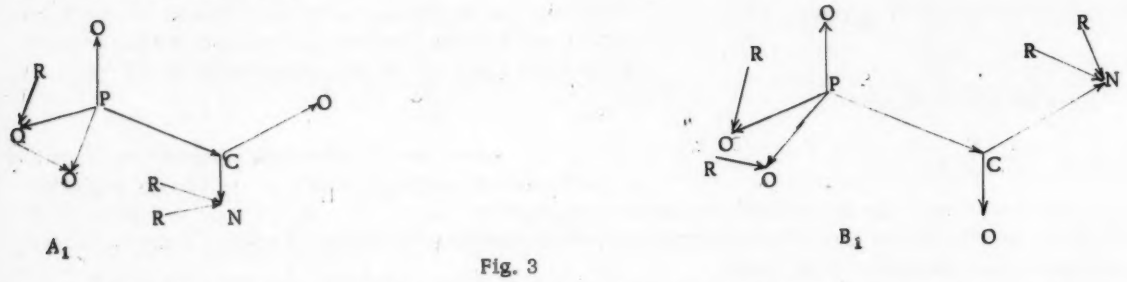

Fig. 3

Thus, if we take into account the interatomic distances and the radius of the sphere of action of Van der Waals forces, which is equal to 2.0 A, we find that the alkoxy groups instead of having free rotation, can have only synchronous vibration about the P–O bond, the O–R groups then being found to lies either in planes perpendicular to the plane of the P–O bond, or in the plane of the P–O bond (Fig. 3 and 4, configurations A_1 and B_1, and A_2 and B_2). The value of the dipole moment averaged over the configurations A_1 and B_1, A_2 and B_2 (in which the two positions described above, for the group $-\overset{\overset{O}{\|}}{C}-N(C_2H_5)_2$ are taken into account) is found to be 3.03 D, differing by 0.07 D from the average experimental value. It is interesting to consider the question of the possible rotation of the group $-\overset{\overset{O}{\|}}{C}-N(C_2H_5)_2$. There are indications in the literature that the group $-N(CH_3)_2$ belongs to the irregular type and may have free rotation at an angle of 74° [7]. The calculations we have carried out for N,N-diethyl(dialkoxyphosphinyl)

formamides taking into account only the position of the $-\overset{\overset{O}{\|}}{C}-N(C_2H_5)_2$- group (configurations A_1 and A_2) give a mean dipole moment of 3.73 D, which is 0.77 D greater than the experimentally found value. Configurations B_1 and B_2 present a second possible position of the $-\overset{\overset{O}{\|}}{C}-N(C_2H_5)_2$- group and give a dipole moment of 2.31 D, which is 0.65 D less than the experimentally found value. If the two positions of the group $-\overset{\overset{O}{\|}}{C}-N(C_2H_5)_2$ are considered to be equally probable, then the experimentally found value will differ from the calculated value by 0.07 D.

Fig. 4

EXPERIMENTAL

The dipole moments of N,N-diethyl(dialkoxyphosphinyl)formamides were determined in benzene solution at 25°. They were calculated according to the formula:

$$\mu = 0.0127 \cdot 10^{-18} \sqrt{(P_T - P_E - P_A) \cdot 298},$$

where P_E is equal to MR_D and is calculated from the Lorentz-Lorenz formula, and P_A is estimated to have five per cent of the value of P_E.

The N,N-diethyl(dialkoxyphosphinyl)formamides were synthesized by Rizpolozhensky and were kindly made available to us for investigation. Before the determinations were made, the substances were purified by distillation (Table 2).

In the calculation of MR_D we used the following values for the refractions of the individual groups: CH_2 4.618; $-O-$ 1.643; O 2.211; the refraction of quinquevalent P was taken as 4.27 units, and the refraction of N in doubly substituted amides was taken as 2.49 units [6].

$(C_2H_5O)_2-\overset{\overset{O}{\|}}{P}OCN(C_2H_5)_2$

C_2	ε_{12}	d_{12}	P_{12}	P_2
0.002167	2.2991	0.8757	27.07	229.9
0.003578	2.3169	0.8764	27.39	238.9
0.005021	2.3351	0.8764	27.72	243.2
0.005905	2.3463	0.8767	28.58	245.9
0.007951	2.3689	0.8791	28.35	242.9
0.009614	2.3930	0.8791	28.73	244.8
0.0000	2.2725	0.8740	26.63	—

$P_T = 236.00$; $P_{A+E} = 59.27$; $P_{Or} = 176.73$;

$\mu = 2.91$ D

SUMMARY

1. Dipole-moment measurements have been made on six N,N-diethyl(dialkoxyphosphinyl)formamides. The mean value obtained for the dipole moments is 2.96 D, which is close to the value calculated on the assumption of free rotation of the irregular groups (μ = 3.33 D).

2. Calculation of the interatomic distances between individual groups in N,N-diethyl(dialkoxyphosphinyl)formamides, taking into account the free rotation of the irregular groups, shows, however, the presence of a great measure of overlap of the spheres of action of Van der Waals forces due to methyl and methylene groups, and this makes it improbable that free rotation of the irregular groups can occur.

3. It is more probable that there is a synchronous vibration of OR and $-\overset{\overset{O}{\|}}{C}N(C_2H_5)_2$ groups, having an amplitude of 180°.

TABLE 2

No.	Substance	B.p. °C	Pressure (mm Hg)	d_4^{25}	n_D^{25}	MR_D found	MR_D calculated
1	$(C_2H_5O)_2-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{P}}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{C}}-N(C_2H_5)_2$	117-119	4	1.0806	1.4470	58.67	58.23
2	$(n\text{-}C_3H_7O)_2-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{P}}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{C}}-N(C_2H_5)_2$	131-132	2	1.0453	1.4478	67.91	67.47
3	$(i\text{-}C_3H_7O)_2-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{P}}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{C}}-N(C_2H_5)_2$	114-115	1.5	1.0339	1.4430	68.01	67.44
4	$(n\text{-}C_4H_9O)_2-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{P}}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{C}}-N(C_2H_5)_2$	148-149.5	2	1.0202	1.4480	76.98	76.70
5	$(i\text{-}C_5H_{11}O)_2-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{P}}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{C}}-N(C_2H_5)_2$	155-155.5	4	0.9963	1.4482	86.54	85.78
6	$(C_6H_{13}O)_2-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{P}}-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{C}}-N(C_2H_5)_2$	183-184.5	3.5	0.9707	1.4458	95.91	95.17

$(n\text{-}C_3H_7O)_2-\underset{\underset{O}{\|}}{P}OCN(C_2H_5)_2$

C_2	i_2	d_{12}	P_{12}	P_2
0.001937	2.2978	0.8742	27.10	263.9
0.003404	2.3196	0.8750	27.51	278.9
0.004299	2.3314	0.8750	27.74	277.9
0.005082	2.3410	0.8757	27.89	272.0
0.007697	2.3765	0.8780	28.49	266.2
0.006839	2.3651	0.8764	28.35	273.2
0.0000	2.2725	0.8730	26.64	–

$P_T = 262.00$; $P_{A+E} = 72.02$; $P_{Or} = 189.98$;

$\mu = 3.02$ D

$(i\text{-}C_3H_7O)_2-\underset{\underset{O}{\|}}{P}OCN(C_2H_5)_2$

C_2	i_2	d_{12}	P_{12}	P_2
0.001907	2.2930	0.8747	27.01	238.5
0.004271	2.3200	0.8751	27.56	246.0
0.002972	2.3030	0.8750	27.22	231.0
0.005916	2.3408	0.8768	27.95	252.7
0.006579	2.3483	0.8767	28.11	253.8
0.008923	2.3764	0.8780	28.80	247.3
0.000	2.2725	0.8742	26.63	–

$P_T = 245.00$; $P_{A+E} = 72.14$; $P_{Or} = 172.86$;

$\mu = 2.88$ D

$(n\text{-}C_4H_9O)_2-\underset{\underset{O}{\|}}{P}OCN(C_2H_5)_2$

C_2	i_2	d_{12}	P_{12}	P_2
0.004052	2.3216	0.87555	27.58	263.7
0.001441	2.2898	0.8738	26.99	279.7
0.002404	2.3025	0.8740	27.24	279.3
0.005448	2.3310	0.8754	27.77	234.6
0.005908	2.3444	0.8760	28.04	265.1
0.007994	2.3733	0.8777	28.57	269.9
0.000	2.2725	0.8736	26.63	–

$P_T = 280.00$; $P_{A+E} = 81.64$; $P_{Or} = 198.36$;

$\mu = 3.09$ D

$(i\text{-}C_5H_{11}O)_2-\underset{\underset{O}{\|}}{P}OCN(C_2H_5)_2$

C_2	i_2	d_{12}	P_{12}	P_2
0.001847	2.2943	0.8742	27.07	267.5
0.002753	2.3035	0.8747	27.28	262.9
0.004602	2.3260	0.8751	27.80	270.0
0.005846	2.3393	0.8759	28.04	266.3
0.007085	2.3550	0.8772	28.06	567.2
0.000	2.2725	0.8735	26.63	–

$P_T = 270.00$; $P_{A+E} = 92.57$; $P_{Or} = 177.43$;

$\mu = 2.92$ D

$$(C_6H_{13}O)_2\text{—}P(O)CN(C_2H_5)_2$$

C_2	n_2	d_{12}	P_{12}	P_2
0.001489	2.2888	0.8735	27.02	282.3
0.004091	2.3198	0.8750	27.67	279.0
0.002480	2.3029	0.8740	27.30	298.0
0.003178	2.3106	0.8743	27.47	288.7
0.005001	2.3301	0.8750	27.91	279.2
0.005645	2.3391	0.8754	28.07	279.9
0.000	2.2725	0.8735	26.63	—

$P_T = 282.00$; $P_{A+E} = 101.77$; $P_{Or} = 180.23$;

$\mu = 2.94$ D

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LITERATURE CITED

[1] B. A. Arbuzov and N. I. Rizpolozhensky, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 5, 847 (1952)*

[2] A. E. Arbuzov and P. I. Rakov, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 3, 237 (1950).

[3] H. Stuart, "The Structure of Molecules", United Sci. Tech. Press, 1937, p. 153.

[4] C. P. Smyth, G. L. Lewis, J. Am. Chem. Soc. 62, 1219, 1531 (1940).

[5] B. A. Arbuzov and T. G. Shavsha, Proc. Acad. Sci. USSR, 79, No. 4, 599 (1951).

[6] K. Fuchs and Wolf, Hand. and Jahrbuch d. chem. Phys. 6, 365 (1938).

[7] I. R. Ruhoff, E. E. Reid, J. Am. Chem. Soc. 59, 401 (1937).

[8] T. G. Shavsha, Sci. Mem. Kazan State Univ., 110, Book 9 (Chemistry), 1950.

* See Consultants Bureau translation, p. 755.

ESTERS OF ALKYLPHOSPHONIC ACIDS, AND THEIR PARACHORS

B. A. Arbuzov and V. S. Vinogradova

The principal methods for the preparation of alkylphosphonic esters are: action of alkyl halides on full phosphorous esters (the A. E. Arbuzov rearrangement), and action of alkyl halides on metal dialkyl phosphites. By these methods a considerable number of different alkylphosphonic esters have been obtained [1]. In our investigations of the parachors of organophosphorus compounds we have found it necessary to prepare alkylphosphonic esters of various types: 1) those having a long-chain hydrocarbon radical attached to phosphorus and short-chain hydrocarbon radicals in the ester groups, 2) those having a short-chain hydrocarbon radical attached to phosphorus, and long-chain hydrocarbon radicals in the ester groups, 3) those having long-chain hydrocarbon radicals in all three positions, and finally 4) those having unlike hydrocarbon radicals in the ester groups. The syntheses of alkylphosphonic esters of these types are described in the present communication.

A considerable number of esters of the first type are described in the literature [2]. In the experimental part of this paper the experimental part of this paper the results are given of the preparation of the diethyl esters of hexyl- and octyl-phosphonic acids by the rearrangement of triethyl phosphite under the action of the alkyl halide; the data given in the literature concerning these preparations are very incomplete [2].

As representatives of the second type we have synthesized esters of methylphosphonic acid. They were prepared both by the action of methyl iodide or dimethyl sulfate on trialkyl phosphites, and also, in certain cases, by the action of methyl iodide on sodium dialkyl phosphite. The constants of the esters obtained are given in Table 1.

Alkylphosphonic esters of the third type, having long hydrocarbon radicals, both attached to phosphorus and also in the ester groups, have not been described. Certain difficulties are met in their preparation. The synthesis of such esters by the action of an alkyl halide on a trialkyl phosphite does not proceed smoothly when the alkyl radicals are large [2]. When the reaction is carried out at moderate temperatures, it may not go to completion, and, owing to the closeness in boiling point of trialkyl phosphite and the isomeric dialkyl alkylphosphonate, their separation may not be complete.

When heating is carried out at high temperatures it is possible, as experiment shows, that decomposition will occur with splitting off of the corresponding olefin. For this reason we carried out parallel syntheses of these esters by the action of alkyl halides on sodium dialkyl phosphites. It must be pointed out that the preparation of substances having closely agreeing constants by the use of the two methods presents difficulty: owing to the high boiling point the use of a fractionating column gives rise to difficulty, and the value obtained for the boiling point of a high-boiling ester varies with design of the distilling flask, particularly with respect to the presence or absence of a small fractionating column when the boiling range is narrow. The constants of the esters obtained are given in Table 2.

Mixed esters of alkylphosphonic acids have not been described in the literature. In order to prepare them we tried the partial transesterification of diethyl alkylphosphonates with the corresponding alcohols. We have previously used this method successfully both for the preparation of esters having identical radicals (trialkyl phosphites, dialkylphosphorous acids [3]), and also for the preparation of dialkylphosphorous acids having unlike alkyl radicals [4]. Experiment showed that transesterification of alkylphosphonic esters did not go in absence of catalysts, but catalysts of acid character, which gave results for trialkyl phosphites and dialkylphosphorous acids, did not give the desired result in the case of alkylphosphonic esters. Transesterification of alkylphosphonic esters occurs, though less readily than in the case of phosphorous esters, in presence of sodium. Using this method we have obtained for the first time the mixed alkylphosphonic esters given in Table 3.

A certain amount of the diester of the higher alcohol was obtained at the same time.

THE PARACHORS OF ALKYLPHOSPHONIC ESTERS

In previous investigations [5] we have examined the parachors of alkylphosphonic acids having radicals ranging from methyl to butyl on phosphorus and on oxygen, and we have found good agreement between the values

found and those calculated assuming the following corrections for chain interaction: corrections for bending at the β-carbons of the ester chains and for parallelism of the ether chains beyond the β-carbon atom, and corrections (β, γ, δ) for the alkyl chain on the phosphorus, which are identical to the corrections for the alkyl chain in a carboxylic ester.

TABLE 1

No.	Formula	B.p. (°C)	Pressure (mm Hg)	d_0^{20}	n_D^{20}	MR_D found	MR_D calculated	γ20
1	$CH_3P(O)(OC_4H_9)_2$	a) 111.0-111.5	5.5	0.9785	1.4240	54.32	54.68	28.2
		b) 105.5-106	5	0.9776	1.4235	54.26	54.68	28.1
2	$CH_3P(O)(OC_6H_{13})_2$	a) 158-159.5	6.5	0.9432	1.4340	72.98	73.15	28.5
3	$CH_3P(O)(OC_8H_{17})_2$	a) 200-200.5	5.5	0.9260	1.4405	91.30	91.62	28.9
4	$CH_3P(O)(OC_{10}H_{21})_2$	a) 227.5-229	4.5	0.9117	1.4435	109.63	110.09	29.3
		b) 206-208.5	0.5	0.9094	1.4420	109.53	110.09	29.4

a) Prepared by the action of methyl iodide on the corresponding trialkyl phosphite.
b) Prepared by the action of methyl iodide or dimethyl sulfate on sodium dialkyl phosphite

TABLE 2

No.	Formula	B.p. (°C)	Pressure (mm Hg)	d_0^{20}	n_D^{20}	MR_D found	MR_D calculated	γ20
1	$C_6H_{13}P(O)(OC_6H_{13})_2$	a) 183.5-184.5	2.5	0.9205	1.4420	96.12	96.24	28.2
		b) 192.0-193.0	6.5	0.9215	1.4410	95.82	96.24	28.2
2	$C_8H_{17}P(O)(OC_8H_{17})_2$	a) 234.5-235	3	0.9034	1.4450	123.37	123.95	28.95
		b) 236.5-237	3.5	0.9028	1.4477	124.0	123.95	29.0
3	$C_9H_{19}P(O)(OC_9H_{19})_2$	a) 214.5-216	0.5	0.8904	1.4450	137.71	137.80	28.5
4	$C_{10}H_{21}P(O)(OC_{10}H_{21})_2$	a) 241.5-243	0.5	0.8946	1.4510	151.30	151.66	29.7
		b) 230.5-231.5	0.07	0.8932	1.4522	151.93	151.66	29.6

a) Prepared via trialkyl phosphite.
b) Prepared via sodium dialkyl phosphite.

The question of the corrections for the interaction of the ether chains with the alkyl radical on the phosphorus has remained open owing to lack of evidence. Our syntheses of various alkylphosphonic esters may give the data required for the elucidation of these matters.

A study of the parachors of the ethyl esters of hexyl- and octyl-phosphonic acids confirmed our previous conclusions concerning the applicability of the corrections β, γ, and δ for the alkyl chain of carboxylic esters to the case of alkylphosphonic esters. In order not to introduce corrections for the alkyl group on the phosphorus, but to study only the interaction of the ester chains, we have determined the parachors of the methylphosphonic esters from dibutyl to didecyl.

TABLE 3

No.	Formula	B.p. (°C)	Pressure (mm Hg)	d_0^{20}	n_D^{20}	MR_D found	MR_D calculated	γ^{20}
1	$CH_3P(O)(OC_2H_5)(OC_6H_{13})$	119-120	8	0.9767	1.4260	54.61	54.68	–
2	$CH_3P(O)(OC_2H_5)(OC_8H_{17})$	134.0-135.0	7	0.9519	1.4312	64.26	63.92	–
3	$CH_3P(O)(OC_2H_5)(OC_{10}H_{21})$	151.0-152.0	4	0.9504	1.4335	72.37	73.15	–
4	$C_6H_{13}P(O)(OC_2H_5)(OC_6H_{13})$	162.5-163.5	9	0.9357	1.4350	77.62	77.77	28.3
5	$C_8H_{17}P(O)(OC_2H_5)(OC_8H_{17})$	192.5-194.0	4	0.9188	1.4412	96.16	96.24	28.8

TABLE 4

No.	Formula	$[P]_{found}$	$[P]_{calcd.}$	Corrections	Discrepancy (%)	Notes
1	$C_6H_{13}P(O)(OC_2H_5)_2$	530.0	532.5	2β(βγδ)	−0.5	–
2	$C_8H_{17}P(O)(OC_2H_5)_2$	611.4	613.0	2β(βγδ)	−0.2	–
3	$CH_3P(O)(OC_4H_9)_2$	490.8	492.4	2β, 2 ||	−0.3	Prepared from dimethyl sulfate
	Ditto	490.3	492.4	2β, 2 ||	−0.4	Prepared from CH_3I and the phosphite
4	$CH_3P(O)(OC_6H_{13})_2$	647.8	649.1	2β, 4 ||	−0.2	–
5	$CH_3P(O)(OC_8H_{17})_2$	802.5	806.1	2β, 6 ||	−0.4	–
6	$CH_3P(O)(OC_{10}H_{21})_2$	964.8	963.8	2β, 8 ||	+0.1	Prepared via the phosphite
	Ditto	961.5	963.8	2β, 8 ||	−0.2	Prepared via sodium didecyl phosphite

The values of [P] (the parachor) found are in agreement with those calculated taking into account corrections for the parallelism of the ester chains beyond the β-carbon atom, as will be seen from the data in Table 4.

The parachors of alkylphosphonic esters can give interesting material concerning the presence of corrections for the interaction of the chains, but there are insufficient accurate data available at the present time for us to form a judgment concerning corrections in parachors of compounds of this type.

TABLE 5

No.	Formula	[P] found	[P] I calcd.	Corrections	Discrepancy (%)	[P] II calcd.	Corrections	Discrepancy (%)	[P] III calcd.	Corrections	Discrepancy (%)
1	$C_6H_{13}P(O)(OC_6H_{13})_2$ a)	836.3	837.4	2β(βγδ) 8	−0.1	846.5	2β(βγδ) 4	−1.2	837.6	2β(βγδ) 8	−0.2
	Ditto b)	836.1	837.4	2β(βγδ) 8	−0.1	846.5	2β(βγδ) 4	−1.2	837.6	2β(βγδ) 8	−0.2
2	$C_8H_{17}P(O)(OC_8H_{17})_2$ a)	1075.0	1067.6	2β(βγδ)14	+0.6	1095.7	2β(βγδ) 6	−0.9	1071.6	2β(βγδ)12	+0.3
	Ditto b)	1076.7	1067.6	2β(βγδ)14	+0.7	1095.7	2β(βγδ) 6	−0.9	1071.6	2β(βγδ)12	+0.4
3	$C_9H_{19}P(O)(OC_9H_{19})_2$	1196.0	1182.9	2β(βγδ)17	+1.0	1205.6	2β(βγδ) 7	−0.8	1189.6	2β(βγδ)14	+0.5
4	$C_{10}H_{21}P(O)(OC_{10}H_{21})_2$	1310.8	1298.8	2β(βγδ)20	+0.9	1325.8	2β(βγδ) 8	−1.1	1307.5	2β(βγδ)16	+0.2
5	$C_6H_{13}P(O)(OC_2H_5)(OC_6H_{13})$	686.0	689.7	2β(βγδ) 2	−0.5	694.0	2β(βγδ)	−1.1	–	–	–
6	$C_8H_{17}P(O)(OC_2H_5)(OC_8H_{17})$	843.7	844.3	2β(βγδ)4	−0.1	855.4	2β(βγδ)	−1.4	–	–	–

In the previous work on the parachors of alkyl phosphonic esters [5], we were unable to resolve the question of the possibility of interaction between all three alkyl chains when they are sufficiently long. The parachor results for didecyl decylphosphonate pointed to interaction between only the two ester chains, but this question cannot be finally settled on the basis of one example only. Also, the preparation of didecyl decylphosphonate by the isomerization of tridecyl phosphite was found to be capricious, and often the product of the isomerization of tridecyl phosphite was found to decompose with separation of decene, which dissolved in the distilled ester and modified its properties. It is evidently from this cause that the constants of the didecyl decylphosphonate previously described by us differ appreciably from those cited in the present communication.

The question of the interaction of chains in alkylphosphonic esters having long radicals on the phosphorus and in the ester groups can be resolved by the determination of the parachors of a series of esters. The values of the parachors obtained for the esters that we have synthesized are given in Table 5.

Under the heading [P] I (calcd.) are given the values of [P] calculated for interaction between all three chains — beyond the β-carbons of the ester chains and beyond the δ-carbon of the alkyl chain on the phosphorus; under [P] II (calcd) — for interaction of only the two ester chains; and under [P] III (calcd.) — for interaction of the two ester chains, but with doubled corrections for parallelism. It will be seen that the experimental values of [P] lie half way between the values calculated for the interaction of three chains([P] I) and those calculated for interaction of the two ester chains ([P] II).

It is difficult to decide at present whether this departure of $[P]_{found}$ is to be explained by the difficulty of preparing these high-boiling esters in a sufficiently high degree of purity for accurate parachor determinations, or whether this nonagreement is to be explained by other causes, and the question of the parachor corrections for chain interaction in alkylphosphonic esters having long alkyl radicals on the phosphorus and in the ester groups remains an open one.

EXPERIMENTAL

Diethyl Methylphosphonate

a) Sodium diethyl phosphite was prepared from diethylphosphorous acid (i.e., the tautomeric mixture of diethyl hydrogen phosphite and diethyl phosphonate — Translator) (35 g) and sodium (6 g) in dry ether (250 ml). Methyl iodide (38 g) was added gradually under cooling (with water). Sodium iodide was not precipitated immediately, and when the addition of methyl iodide was complete the mixture was heated under reflux for 2 hrs 30 min. After separation of the sodium iodide (23 g) and removal of ether, vacuum distillation yielded diethyl methylphosphonate (20 g) of b.p. 80°/13 mm; n_D^{20} 1.4110; d_0^{20} 1.0548. A thick clear mass, soluble in water, remained behind in the flask.

b) Dimethyl sulfate (32 g) was added gradually under cooling to an ethereal solution of sodium diethyl phosphite prepared from diethylphosphorous acid (35 g) and sodium (6 g). Reaction was vigorous. When reaction was nearly complete the flask was heated on a water bath for 90 minutes. The precipitate was filtered off (31 g). The product obtained after removal of ether and distillation was diethyl methylphosphonate (34 g), b.p. 75-76°/10 mm, n_D^{20} 1.4092; d_0^{20} 1.0763. It is evident that the ester contained a small amount of dimethyl sulfate, which has a similar boiling point.

Dibutyl Methylphosphonate

a) A solution of sodium butoxide was prepared from sodium (5 g) and butyl alcohol, dibutylphosphorous acid (40 g) was added, and then dimethyl sulfate (26 g) was introduced slowly. Reaction was vigorous, and a voluminous precipitate formed, which did not settle on standing. A small amount of clear solution was obtained by centrifugation, and after removal of the alcohol and vacuum distillation it yielded dibutyl methylphosphonate (11 g) having the following constants: b.p. 105.5-106° at 5 mm, n_D^{20} 1.4235; d_0^{20} 0.9776; calculated MR_D 54.68; found MR_D 54.26; γ^{20} 28.1.

b) A mixture of tributyl phosphite (15 g) and methyl iodide (12 g, the theoretical amount is 8.6 g) was sealed in a tube. The tube was heated for four hours at 155-165° and for 2 hrs 30 min at 170-195°. Methyl iodide (4 g) and butyl iodide (10 g, b.p. 130°/755 mm) were distilled off, and vacuum distillation yielded dibutyl methylphosphonate (9 g, 72%) as a colorless liquid having the following constants: b.p. 111-111.5° at 5.5 mm; n_D^{20} 1.4240; d_0^{20} 0.9785; found MR_D 54.32; calculated MR_D 54.68; γ^{20} 28.2.

Found %: P 14.75
$C_9H_{21}O_3P$. Calculated %: P 14.88

Preparation of Dihexyl Methylphosphonate

A mixture of trihexyl phosphite (11.5 g) and methyl iodide [8 g (theory requires 4.8 g)] was sealed in a tube, which was then heated for four hours at 170-180°. Fractionation yielded methyl iodide (2 g), hexyl iodide (5 g), and a fraction of b.p. 156-180°/6 mm. The last was distilled from a flask having a small fused-on Widmer column [6] and yielded a fraction (4.5 g) having the following constants: b.p. 158-159.5° at 6.5 mm; d_0^{20} 0.9432; n_D^{20} 1.4340; found MR_D 72.98; calculated MR_D 73.15; γ^{20} 28.5.

Found %: P 11.78
$C_{13}H_{29}O_3P$. Calculated %: P 11.72

Preparation of Dioctyl Methylphosphonate

A mixture of trioctyl phosphite (17 g) and methyl iodide [10 g (theory requires 5.8 g)] was sealed in a tube, which was then heated for 3 hrs 30 min at 170-185°. Fractionation yielded methyl iodide (3.5 g), some octyl iodide, and dioctyl methylphosphonate (8 g) having the following constants: b.p. 200-200.5°/5.5 mm; d_0^{20} 0.9260; n_D^{20} 1.4405; found MR_D 91.30; calculated MR_D 91.62; γ^{20} 28.9

Found %: P 9.82
$C_{17}H_{37}O_3P$. Calculated %: P 9.76

Didecyl Methylphosphonate

a) A mixture of tridecyl phosphite (11.5 g) and methyl iodide [6 g(theory requires 3 g)] was sealed in a tube, which was then heated for four hours at 160-165° and for 3 hrs 30 min at 170-195°. Fractionation yielded methyl iodide (2.8 g), some decyl iodide of b.p. 118°/5.5 mm, and didecyl methylphosphonate (3.5 g) having

the following constants: b.p. 227.5-229° at 4.5 mm; d_0^{20} 0.9117; n_D^{20} 1.4435; found MR_D 109.63; calculated MR_D 110.09; γ^{20} 29.3.

Found %: P 8.20

$C_{21}H_{45}O_3P$. Calculated %: P 8.23

The ester was a colorless oil.

b) Sodium didecyl phosphite was prepared in a medium of ligroin (b.p. 75-110°) from didecylphosphorous acid (21 g) and sodium (1.3 g). When the mixture was heated on the water bath, the sodium reacted vigorously. The reaction finally slowed down, and the sodium was floated off, extracted, and flattened out, after which it again reacted when the mixture was warmed. The amount of unchanged sodium was 0.2 g. Methyl iodide (9 g) was added, and sodium iodide was precipitated and was removed by centrifugation. The liquid frothed strongly when the ligroin was distilled off. Vacuum fractionation yielded a fraction of b.p. 198-213°/1 mm; a large amount of residue residue remained in the flask. In a second fractionation a didecyl methylphosphonate fraction was obtained (in negligible amount); it had the following constants: b.p. 206-208.5° at 0.5 mm; d_0^{20} 0.9094; n_D^{20} 1.4420; found MR_D 109.53; calculated MR_D 110.09; γ^{20} 29.4.

Found %: P 8.50

$C_{21}H_{45}O_3P$. Calculated %: P 8.23

Ethyl Hexyl Methylphosphonate

Diethyl methylphosphonate (20 g) and hexyl alcohol (20 g) were placed in a flask having a small fused-on Widmer fractionating column, and a small piece of sodium was added. At a bath temperature of 175-180° ethanol started to come over. After some time the distillation of alcohol slowed down considerably: more sodium was added, and distillation of alcohol started up again. The total amount of sodium added was 0.2 g, and the amount of alcohol distilled off was 5.5 ml. Fractionation yielded a small amount of low-boiling fractions, hexyl alcohol, and fractions having boiling points of 120-124°/9 mm and 155-160°/8 mm. A second distillation of the fraction of b.p. 120-124°/9 mm yielded ethyl hexyl methylphosphonate (9.5 g) having the following constants: b.p. 119-120° at 8 mm; d_0^{20} 0.9767; n_D^{20} 1.4260; found MR_D 54.61; calculated MR_D 54.68.

Found %: P 14.47

$C_9H_{21}O_3P$. Calculated %: P 14.87.

A second distillation of the fraction of b.p. 155-160° yielded dihexyl methylphosphonate (3 g) having b.p. 158.5-160° at 8 mm; d_0^{20} 0.9441; n_D^{20} 1.4300.

Ethyl Octyl Methylphosphonate

Diethyl methylphosphonate (17 g), octyl alcohol (18 g), and a small piece of sodium (0.05-0.1 g) were placed in a flask having a Widmer fractionating column. Alcohol started to come over at a bath temperature of 190°; the bath was maintained at 205-210°, and was heated toward the end to 218°. In the course of four hours 6 ml of alcohol came over. Toward the end a small amount of white precipitate formed in the flask. Distillation yielded octyl alcohol (b.p. 65-130°/9 mm), a fraction (15 g) of b.p. 130-155°/10 mm, and a fraction of b.p. 175-177°/2 mm. In the redistillation of the fraction of b.p. 130-155°/10 mm, practically the whole came over a range of one degree, giving ethyl octyl methylphosphonate (6 g) having the constants: b.p. 134-135.5° at 7 mm; d_0^{20} 0.9519; n_D^{20} 1.4312; found MR_D 64.26; calculated MR_D 63.92.

Found %: P 12.77

$C_{11}H_{25}O_3P$. Calculated %: P 13.11

The fraction of b.p. 175-177°/2 mm was dioctyl methylphosphonate (3.5 g). After being redistilled it had b.p. 202-204°/7 mm; d_0^{20} 0.9269; n_D^{20} 1.4380.

Decyl Ethyl Methylphosphonate

Diethyl methylphosphonate (16 g) and decyl alcohol (20 g) were placed in a flask having a Widmer fractionating column, and sodium (0.05-0.1 g) was added. Alcohol began to come over at a bath temperature of 165°; the temperature was maintained at 215-220°, and, when distillation of alcohol was nearly complete, it was raised to 225°. In the course of four hours, 5.5 ml of alcohol came over; a small amount of white precipitate formed in the flask. The following fractions were obtained, on distillation:

Fraction I, b.p. 72-145°/9 mm

Fraction II, b.p.145-155°/5 mm

Fraction III, b.p.155-230°/5 mm

Redistillation of Fractions II and III yielded decyl ethyl methylphosphonate (10 g) having the constants: b.p. 151-152°/4 mm; n_D^{20} 1.4325; d_0^{20} 0.9504; found MR_D 72.37; calculated MR_D 73.15.

Found %: P 11.83

$C_{13}H_{29}O_3P$. Calculated %: P 11.72

From the high-boiling fractions didecyl methylphosphonate (4 g) was isolated; it had the following constants: b.p. 226.5-227.5 at 5 mm; n_D^{20} 1.4430; d_0^{20} 0.9177.

Ethyl Hexyl Hexylphosphonate

The diethyl hexylphosphonate required for the transesterification reaction was obtained by the action of hexyl bromide on triethyl phosphite [2]. The triethyl phosphite (20 g) and hexyl bromide (25 g) were placed in a flask having a small fractionating column, and the flask was heated in a bath of Wood's metal. Ethyl bromide began to come over at a bath temperature of 160°, and, towards the end of the distillation, the bath temperature was 200°. Distillation of the residue yielded hexyl bromide (6 g) and diethyl hexylphosphonate, which, after being redistilled twice, had the constants: b.p. 123.5-125.5/8.5 mm; d_0^{20} 0.9659; n_D^{20} 1.4295.

Transesterification of Diethyl Hexylphosphonate with Hexyl Alcohol

Transesterification does not proceed in absence of catalyst; neither phosphoric acid nor camphorsulfonic acid will act as a catalyst, but the reaction proceeds in presence of sodium. Diethyl hexyl phosphonate (12 g) and hexyl alcohol (15 g) were placed in a flask having a small fractionating column, and a small piece of sodium was added. Alcohol began to come over at a bath temperature of 180-190°; 3.5 ml came over. Vacuum distillation yielded hexyl alcohol, b.p. 62-65°/9 mm, and the fractions:

Fraction I, b.p. 125-137°/9 mm

Fraction II, b.p. 139-147°/8 mm

Fraction III, b.p.189-192°/8 mm

As a result of several refractionations of these fractions, ethyl hexyl hexylphosphonate (5 g) was obtained. It had the constants: b.p.162.5-163.5°/9 mm; d_0^{20} 0.9357; n_D^{20} 1.4350; found MR_D 77.62; calculated MR_D 77.77; γ^{20} 28.3.

Found %: P 11.04, 10.93

$C_{14}H_{31}O_3P$. Calculated %: P 11.1

In each refractionation, evidently owing to disproportionation, a further amount of fraction of b.p. 162.5-163.5°/9 mm was obtained.

Ethyl Octyl Octylphosphonate

The diethyl octylphosphonate required for the transesterification reaction was obtained by the action of octyl bromide (27 g) on triethyl phosphite (18.8 g) [2]. Ethyl bromide was driven off at a bath temperature of up to 200° (at the end of the reaction); 4.5 ml of ethyl bromide was driven off. Distillation yielded octyl bromide, b.p. 85-90°/11 mm and a fraction of b.p. 145-152°/10 mm. From the latter fraction there was obtained diethyl octylphosphonate (18 g) having the constants: b.p. 149.5-150.5°/10 mm; d_0^{20} 0.9490; n_D^{20} 1.4335; γ^{20} 28.7

Diethyl octylphosphonate (13 g), octyl alcohol (17 g), and sodium (0.1 g) were placed in a flask having a small Widmer fractionating column. Ethyl alcohol began to distill at a bath temperature of 200°, and 2.5 ml came over in the course of five hours; toward the end the bath temperature was 215°. Distillation yielded octyl alcohol (11.5 g), a fraction of b.p. 85-185°/9 mm (2.5 g), and a fraction of b.p. 185-200°/4 mm; distillation was accompanied by considerable frothing.

By distillation of the higher fraction, ethyl octyl octylphosphonate was isolated in very small amount; it had the constants: b.p. 192.5-194° at 4 mm; d_0^{20} 0.9188; n_D^{20} 1.4412; found MR_D 96.16; calculated MR_D 96.24; γ^{20} 28.8

Found %: P 9.30, 9.20

$C_{18}H_{39}O_3P$. Calculated %: P 9.26.

The ester is a viscous yellowish liquid.

Dihexyl Hexylphosphonate

a) Dihexyl hexylphosphonate was obtained by the A.E.Arbuzov isomerization of trihexyl phosphite (b.p.171-173°/5 mm) in presence of hexyl bromide (b.p. 47.5-48°/15 mm). Trihexyl phosphite (7 g) was heated with hexyl bromide (1.5 g) in a flask fitted with an air condenser for seven hours, the bath temperature being 160-200°. In the course of vacuum distillation, first hexyl bromide came over, then a certain amount of decomposition occurred, and finally dihexyl hexylphosphonate came over; it had b.p. 183.5-184.5°/2.5 mm; n_D^{20} 1.4420; d_0^{20} 0.9205; found MR_D 96.12; calculated MR_D 96.24; γ^{20} 28.2.

Found %: P 9.32, 9.13

$C_{18}H_{39}O_3P$. Calculated %: P 9.24

b) Dihexylphosphorous acid was obtained by the action of PCl_3 (14 g) on hexyl alcohol (31 g) under cooling with snow. Hydrogen chloride was removed by suction. Distillation yielded hexyl chloride (8 g; b.p. 134-135°) and dihexylphosphorous acid (19 g, 76%), b.p. 153-155°/6 mm, n_D^{20} 1.4340.

A solution of sodium dihexyl phosphite was obtained from dihexylphosphorous acid of b.p. 153-155°/6 mm (19 g), sodium (1.7 g), and benzene (100 ml); the sodium was consumed completely in a three-hour heating on the water bath. Hexyl bromide (13 g; b.p. 66°/34 mm) was added gradually to the solution obtained, and the flask was again heated for 3 hours 30 min. The colloidal precipitate of sodium bromide that formed during the reaction was washed out by shaking the mass carefully with water in a separating funnel; this operation was repeated. The benzene solution obtained was dried with calcium chloride, the benzene was distilled off, and the residue was vacuum-distilled. A small amount of hexyl bromide was obtained, and a fraction of b.p. 178-180°/2 mm was isolated. There was a thick residual mass of sodium dihexyl phosphite. Redistillation yielded a substance of b.p. 192-193°/6.5 mm; n_D^{20} 1.4410; d_0^{20} 0.9215; found MR_D 95.82; calculated MR_D 96.24; γ^{20} 28.2.

Found %: P 8.90, 9.23

$C_{18}H_{39}O_3P$. Calculated %: P 9.24

Dioctyl Octylphosphonate

Dioctyl octylphosphonate was prepared by two methods:

a) It was prepared, analogously to dihexyl hexylphosphonate, by isomerization of trioctyl phosphite (16 g; b.p. 212-214°/2 mm) in presence of octyl bromide (2.5 g; b.p. 196-197.5°). The mixture was heated for 12 hours, the bath temperature being 160-200°. Toward the end a yellowish coloration occurred in the liquid. In the vacuum distillation, first octyl bromide came over, then, when distillation of the ester began, considerable decomposition occurred, after which the following fractions were obtained:

Fraction I, b.p. 223-227°/3 mm

Fraction II, b.p. 234.5-236.5°/3.5-4 mm

Redistillation yielded the ester, which had b.p. 234.5-235°/3 mm; n_D^{20} 1.4450; d_0^{20} 0.9034; found MR_D 123.37; calculated MR_D 123.95; γ^{20} 28.9.

Found %: P 7.39, 7.35

$C_{24}H_{51}O_3P$. Calculated %: P 7.40

b) A solution of sodium dioctyl phosphite was obtained from dioctylphosphorous acid (14.5 g) (which was obtained by transesterification of diethylphosphorous acid), sodium (1.0 g), and benzene (150 ml); octyl bromide (9 g) was added to this solution in portions. Reaction was completed by heating the mixture on a water bath for 3 hours. The sodium bromide formed did not settle; it was precipitated by adding water (0.5 ml) and centrifuging. The benzene solution was dried with calcium chloride, and the benzene was driven off. As a result of three distillations, dioctyl octylphosphonate (7 g) was obtained; it had the constants: b.p. 236.5-237° at 3 mm; d_0^{20} 0.9028; n_D^{20} 1.4477; found MR_D 124.0; calculated MR_D 123.95; γ^{20} 29.0.

Found %: P 7.69

$C_{24}H_{51}O_3P$. Calculated %: P 7.40

Dinonyl Nonylphosphonate

This was prepared by isomerization of trinonyl phosphite of b.p. 186.5-188°/0.018 mm (9 g) in presence of nonyl bromide of b.p. 80-81°/5.5 mm (2 g). Heating was for 7 hours at a bath temperature of 160-200°; the liquid in the flask became somewhat yellow. Nonyl bromide was distilled off, and after slight decomposition the ester followed (b.p. 214.5-216°/0.5 mm), leaving negligible residue; it had constants: n_D^{20} 1.4450; d_0^{20} 0.8904; found MR_D 137.71; calculated MR_D 137.80; γ^{20} 28.5.

Found %: P 6.60; 6.64. $C_{27}H_{57}O_3P$. Calculated %: P 6.73.

Didecyl Decylphosphonate

a) The ester was obtained by the isomerization reaction: tridecyl phosphite of b.p. 250-252°/(uncorrected) 2.5 mm (13 g) was heated with decyl bromide of b.p. 122-123°/18 mm (3 g) for 16 hours at a bath temperature of 160-200°; the material yellowed strongly. After a small amount of decyl bromide had been distilled off, there was some considerable decomposition; some distillate was obtained by use of the mercury pump: b.p. 241.5-243°/0.5 mm (it was not found possible to obtain a greater rarefication in the distillation). Finally, considerable decomposition set in; a residue remained in the flask. The constants of the ester obtained were: n_D^{20} 1.4510; d_0^{20} 0.8946; found MR_D 151.30; calculated MR_D 151.66; γ^{20} 29.7.

Found %: P 6.56, 6.48

$C_{30}H_{63}O_3P$. Calculated %: P 6.16

b) Didecylphosphorous acid was obtained by the action of phosphorus trichloride on decyl alcohol. The phosphorus trichloride was added dropwise to the decyl alcohol (24 g), and hydrogen chloride was drawn off under suction at room temperature. Distillation yielded decyl chloride of b.p. 67-69°/9 mm (8 g) and didecylphosphorous acid of b.p. 188-194°/0.5 mm (15 g, 85%).

Action of decyl bromide on sodium didecyl phosphite. A solution of sodium didecyl phosphite was prepared from didecylphosphorous acid (14 g), sodium (0.9 g), and benzene (100 ml), and decyl bromide (8.7 g) was added. No sodium bromide came down. The mixture was heated under reflux for 5 hours: there was much frothing, but it gradually subsided. The emulsion formed did not readily settle out; ether and sodium chloride were added. The ether–benzene solution was dried with calcium chloride, and the ether and benzene were driven off. Distillation yielded didecyl decylphosphonate, b.p. 234-235°/0.8 mm (11 g). After being redistilled, the ester had the constants: b.p. 230.5-231.5°/0.07 mm; d_0^{20} 0.8932; n_D^{20} 1.4522; found MR_D 151.93; calculated MR_D 151.66; γ^{20} 29.6.

SUMMARY

1. The following alkylphosphonic esters have been synthesized: dibutyl, dihexyl, dioctyl, and didecyl methylphosphonates; dihexyl hexylphosphonate, dioctyl octylphosphonate, dinonyl nonylphosphonate, and didecyl decylphosphonate.

2. Mixed esters of alkylphosphonic acids have been obtained for the first time by a transesterification reaction: ethyl hexyl, ethyl octyl, and ethyl decyl methylphosphonates; ethyl hexyl hexylphosphonate; and ethyl octyl octylphosphonate.

3. The parachors of the alkylphosphonic esters have been determined, and conclusions have been reached concerning the corrections for chain interaction.

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LITERATURE CITED

[1] V.Plets. Organic Compounds of Phosphorus, Defence Industry Press, 1940; G. Kosolapoff. Organophosphorus Compounds, 121-125 and 148-151.

[2] A.H.Ford-Moore, and J.H.Williams. J.Chem.Soc., 1465 (1947); G.Kosolapoff. J.Am.Chem.Soc., 67, 1180 (1945).

[3] B.A.Arbuzov and V.S.Vinogradova. Bull.Acad.Sci.USSR, Div.Chem.Sci., 733 (1951); V.S.Vinogradova. Sci. Mem. Kazan Univ. 110, Book 9, 67 (1950).

[4] B.A.Arbuzov and V.S.Vinogradova. Proc.Acad.Sci.USSR, 83, 79 (1952); G.Kosolapoff. J.Am.Chem.Soc., 73, 49, 89 (1951).

[5] B.A.Arbuzov and V.S.Vinogradova. Bull.Acad.Sci.USSR., Div.Chem.Sci., 459 (1947); V.S.Vinogradova. Sci. Mem. Kazan Univ., 110, Book 9, 24 (1950).

[6] K.Bernkhauer. Introduction to Laboratory Technique in Organic Chemistry, United Sci.Tech.Press, p. 72 (1935).

CERTAIN ALKYLPHOSPHONOTHIONIC, ALKYLPHOSPHONOSELENONIC, DIALKYLPHOSPHINIC, AND ALKYLPHOSPHONOUS ESTERS, AND THE MECHANISM OF ADDITION TO ALKYLPHOSPHONOUS ESTERS

A. I. Razumov, O. A. Mukhacheva, and Sim-Do-Khen

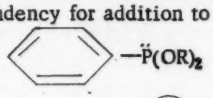
We have been concerned in recent years with the study of certain peculiar properties of various derivatives of alkylphosphonic acids, and have obtained rather interesting results. It was desirable to extend the work to the corresponding properties of the thio analogs of these compounds, in particular alkylphosphonothionic esters, which can be prepared by addition of sulfur to alkylphosphonous esters, $RP(OR)_2$. It was to be expected that addition of sulfur to such esters would proceed fairly readily. A. E. Arbuzov has pointed out in one of his papers [1] that replacement of OR by R in esters of the type $P(OR)_3$ should lead to an increase in the readiness with which addition reactions occur, and also in the readiness with which isomerization (or rearrangement) reactions occur, since these latter reactions proceed the more readily (other things being equal), the greater the tendency for addition to occur.

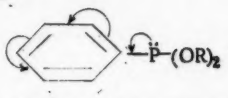
A. E. Arbuzov established a clearly defined parallelism between the rates of sulfur addition to certain tervalent phosphorus compounds and isomerization reactions. Hence, it was to be expected that not only would the ease of sulfur addition be greater for alkylphosphonous esters than for esters of the type $P(OR)_3$, but also the rate of isomerization would be greater. Actually, as will be seen later, the alkylphosphonous esters that we have synthesized have an extremely high tendency to undergo addition reactions and show a greater readiness to undergo isomerization than esters of the types $P(OR)_3$ and $ArP(OR)_2$. At the same time, A. E. Arbuzov remarks in his paper that the question of the cause of the increase in isomerization rate in the phosphorous ester series remains an open one. We consider that the tendency to undergo addition, and hence also, to a certain extent, isomerization, can be explained as follows. Addition reactions at tervalent P are obviously dependent on the presence there of an unshared pair of electrons and also on the nature of the substituents on the phosphorus atom. When the inductive effect of the substituent becomes more negative, or less positive, the tervalent phosphorus compound will become less inclined to undergo addition reactions. Hence the tendency of tervalent P to undergo addition reactions should diminish along the series:

$$R_3P > R_2P(OR) > RP(OR)_2 > P(OR)_3,$$

where R is an aliphatic radical.

On the other hand, the presence of a coordinately unsaturated atom having multiple bonds adjacent to the tervalent P must reduce the tendency for addition to occur at the phosphorus atom. Thus, in the compound



a displacement of electrons is possible  , and consequently arylphosphonous esters should have a lower tendency to undergo addition than the corresponding alkylphosphonous esters, other things being equal: $RP(OR)_2 > ArP(OR)_2$.

Actually, comparative observations on the alkylphosphonous esters that we have synthesized indicate that they undergo addition reactions with sulfur and halogens and undergo the isomerization reaction considerably more readily than esters of the types $P(OR)_3$ and $ArP(OR)_2$. Thus, A. E. Arbuzov brought about addition of bromine to the ester $P(OC_4H_9)_3$-i by slow addition of dry bromine at ordinary temperature. However, for the ester $C_4H_9P(OC_4H_9)_2$-i, for example, the analogous reaction is difficult to carry out at ordinary temperature, and usually considerable cooling (to -15° or -20°) is necessary in order to preserve the reaction products. A.E. Arbuzov generally carried out addition of sulfur to esters of the type $P(OR)_3$ in carbon disulfide solution. For esters of the type $RP(OR)_2$, we used benzene as solvent, but sulfur, and also selenium, readily added also in absence of solvent, in both cases with considerable evolution of heat. A similar situation is found for the isomerization reaction. The esters $C_2H_5P(OC_2H_5)_2$ and $C_4H_9P(OC_4H_9)_2$-i isomerize considerably more readily and rapidly than the corresponding phosphorous esters. Thus, A.E. Arbuzov has shown that five hours' heating at 160° is required for the isomerization of the ester $P(OC_4H_9)_3$-i, whereas isomer-

ization of the ester $C_4H_9P(OC_4H_9)_2$-i requires only three hours at 100°, other conditions being the same.

As would be expected, the ester $C_2H_5P(OC_2H_5)_2$ isomerizes still more readily; two hours at 70° is sufficient. These experiments confirm the explanation given above of the causes of the higher rates of addition reactions for compounds of the type $RP(OR)_2$, as compared with those of the type $P(OR)_3$.

Alkylphosphonous esters were prepared from the corresponding alkylphosphonous dichlorides [2,3] in yields of up to 85% by the action of the corresponding alcohol in presence of a base:

$$RPCl_2 + 2ROH + 2C_5H_5N \longrightarrow RP(OR)_2 + 2C_5H_5N \cdot HCl.$$

Aliphatic esters of alkylphosphonous acids have not been described in the literature and so present interest on their own account. Also, they may be used as starting materials for the preparation of the required alkylphosphonothionic esters. The following esters were prepared:

$$C_2H_5P(OC_2H_5)_2 \text{ and } i\text{-}C_4H_9P(OC_4H_9)_2$$

These are mobile liquids of characteristic, unpleasant odor which combine vigorously with the oxygen of the air. By taking advantage of the tendency, already discussed, of esters of the type $RP(OR)_2$ to undergo addition reactions, we obtained the desired alkylphosphonothionic esters (addition of sulfur):

$$C_2H_5\underset{\underset{S}{\|}}{P}(OC_2H_5)_2 \text{ and } i\text{-}C_4H_9\underset{\underset{S}{\|}}{P}(OC_4H_9)_2.$$

The yields obtained of these esters were almost quantitative. They are colorless liquids of rather pleasant odor. Only one ester of this type appears in the literature: $i\text{-}C_5H_{11}\underset{\underset{S}{\|}}{P}(OC_2H_5)_2$, described in the last century by Guichard [4]. Hydrolysis of the alkylphosphonothionic esters gave the corresponding acids as paraffinlike products; our study of these is not complete.

In the method described for the preparation of alkylphosphonothionic esters, it will be seen that alkylphosphonous esters are required as starting materials. These substances are difficult to work with, for they react very readily with the oxygen of the air. In order to avoid this stage in the preparation of the esters, we have tried also another method for their preparation: sulfur was caused to add directly to an alkylphosphonous dichloride:

$$RPCl_2 + S \longrightarrow R\underset{\underset{S}{\|}}{P}Cl_2$$

and chlorine was then replaced by alkoxy either by the action of alkoxide or by treatment with the alcohol in presence of a tertiary base.

The addition of sulfur to an alkylphosphonous dichloride has been effected previously by Guichard [4]: he heated these substances together in a sealed tube at 125°. He gave no indication of the yields. We have brought about the reaction much more readily by heating the alkylphosphonous dichloride with sulfur in a flask fitted with reflux condenser for one hour in presence of a catalyst ($AlCl_3$). The yields were almost quantitative.

Replacement of chlorine in the alkylphosphonothionic dichloride by the alkoxy group is preferably carried out by the action of the alkoxide, for by the action of the alcohol products of unpleasant odor are obtained and an additional wash with water is necessary (they then show a slight acid reaction, but do not differ appreciably in their constants from the esters prepared by the other method).

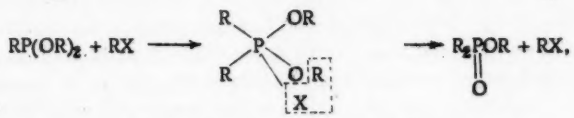
Selenium combines with alkylphosphonous esters with equal ease, an appreciable amount of heat being evolved; in this way we prepared esters of alkylphosphonoselenonic acids, which have not been described previously. We used "metallic" selenium that had been ground to a powder, and this combined with the esters both in a solvent, and in absence of solvent, according to the equation:

$$RP(OR)_2 + Se \longrightarrow R\underset{\underset{Se}{\|}}{P}(OR)_2.$$

The isomerization of alkylphosphonous esters proceeds very readily, as stated above; the reaction follows the Arbuzov scheme:

TABLE

No.	Formula	B.p. (°C)	Pressure (mm Hg)	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	Yield %
1	$i\text{-}C_4H_9PCl_2$	48.5-49	12	1.1720	1.4719	38.54	38.15	26
2	$C_2H_5P(S)Cl_2$	82.5	45.5	1.3550	1.5413	–	–	80
3	$C_2H_5P(OC_2H_5)_2$	137-139	760	0.9064	1.4222	42.0	41.33	60
4	$i\text{-}C_4H_9P(OC_4H_9\text{-}i)_2$	105.5-107.5	12.5	0.8677	1.4290	69.20	69.04	85
5	$C_2H_5P(S)(OC_2H_5)_2$	86.5-87	12	1.0349	1.4617	–	–	80
6	$i\text{-}C_4H_9P(S)(OC_4H_9\text{-}i)_2$	135.5-136	12	0.9636	1.4420	–	–	Quantitative
7	$C_2H_5P(Se)(OC_2H_5)_2$	97.5	11	1.2743	1.4872	–	–	75
8	$i\text{-}C_4H_9P(Se)(OC_4H_9\text{-}i)_2$	144-146	14	1.084	1.4571	–	–	90
9	$(C_2H_5)_2POC_2H_5$ (O)	91-92	14	0.9964	1.4301	38.89	39.13	65
10	$(i\text{-}C_4H_9)_2POC_4H_9\text{-}i$ (O)	99-102	3	0.9151	1.4311	66.21	66.47	80
11	$(C_2H_5)_2PCl$ (O)	108-109.5	16	1.1394	1.4647	34.07	33.59	70
12	$C_2H_5P(S)(OH)_2$	Paraffinlike substance	–	–	–	–	–	–
13	$i\text{-}C_4H_9P(S)(OH)_2$	Ditto	–	–	–	–	–	–
14	$C_2H_5P(O)OH$	"	–	–	–	–	–	–
15	$(i\text{-}C_4H_9)_2P(O)OH$	"	–	–	–	–	–	–



In this way we prepared dialkylphosphinic esters that have not been described previously.

Dialkylphosphinic esters readily react with phosphorus pentachloride with formation of dialkylphosphinic chlorides: $R_2P(O)Cl$.

Hydrolysis of the dialkylphosphinic esters yielded the corresponding acids as paraffinlike products, the study of which has not been completed. One of these acids $(i\text{-}C_4H_9)_2POH$ is described in the literature [5] as an oily liquid.

The substances that we have synthesized are given with their constants in the table.

Note. The atomic refraction of P in alkylphosphonous derivatives is taken to be 7.04.

EXPERIMENTAL

1. Synthesis of Diethyl Ethylphosphonite. The materials taken for reaction were: ethylphosphonous dichloride (50 g), ethanol (35 g), and pyridine (60 g). The same experimental conditions were used as in the preparation of the isobutyl compound [2]. The yield of pure product was 34 g (60%), and it had b.p. 137-139°; d_0^{20} 0.9064; n_D^{20} 1.4222; found MR_D 42.0; calculated MR_D 41.33: This ester is a colorless liquid of unpleasant odor. It combines very readily with the oxygen of the air—much more readily than its isobutyl homolog. It is readily soluble in benzene and ether, and in a number of other organic solvents.

Found %: P 20.24; 20.38

$C_6H_{15}PO_2$. Calculated %: P 20.66

2. Addition of Bromine to Diethyl Ethylphosphonite. The ester (1.1 g) was placed in a test tube cooled with snow and salt, and carbon dioxide was passed continuously. Bromine was then added until a slight yellow color persisted (1.09 g of bromine; theory requires 1.17 g). Cuprous bromide gives a crystalline compound with diethyl ethylphosphonite.

3. Synthesis of Diethyl Ethylphosphonothionate. Diethyl ethylphosphonite (24.4 g) was placed in a flask fitted with reflux condenser and stirrer. Five times this amount of dry benzene was added, and a stream of carbon dioxide was passed. Sulfur (5.2 g) was then added in small portions at a time, the temperature of the mixture being regulated by the rate of sulfur addition so that it did not exceed 60°. The benzene was driven off, and the product was fractionally distilled. The ester (9.7 g, 64.5%; b.p. 86.5-87°/12 mm; d_0^{20} 1.0349; n_D^{20} 1.4617) is a colorless liquid that fumes in air and has a pleasant, refreshing odor. It is only slightly soluble in water.

Found %: S 17.79; 17.64

$C_6H_{15}O_2PS$. Calculated %: S 17.58.

Hydrolysis of the ester, and also of the corresponding phosphonothionic dichloride, yielded the acid—a paraffinlike substance.

4. Synthesis of Ethyl Diethylphosphinate. Diethyl ethylphosphonite (15 g) and ethyl iodide (15.5 g) were heated together in a sealed tube at 70°, heating being interrupted every hour in order to enable any change in the volume of liquid to be noted. After two hours the volume did not change further. Ethyl iodide was driven off, and the residue was vacuum-distilled, yielding a colorless liquid (9.7 g, 64.5%) having a pleasant but faint odor. It had b.p. 91-92°/14 mm, d_0^{20} 0.9964; n_D^{20} 1.4301; MR_D 38.89, calculated MR_D 39.13.

Found %: P 20.28; 20.72

$C_6H_{15}O_2P$. Calculated %: P 20.66

5. Addition of Sulfur to Ethylphosphonous Dichloride. Ethylphosphonous dichloride (22 g) was introduced into a three-necked flask fitted with reflux condenser, stirrer, and a tube, through which either carbon dioxide or nitrogen was passed. The temperature was measured by a thermometer that was immersed in the liquid. Sulfur (5.5 g) was added (in one lot), and the reaction mixture was brought to the boil (112°). Stirring was continued until all the sulfur had dissolved. Heating was then discontinued, stirring was stopped, and a mixture of aluminum chloride (0.6 g) and sulfur (0.2 g) was added rapidly. A violent reaction set in, and the temperature rose to 150°. The mass was heated further for two hours, and the final temperature was 172° (it did not rise above this value). The product was vacuum-distilled, yielding a colorless liquid having a pungent odor (22 g 80%). It had a b.p. 82.5°/45.5 mm, d_0^{20} 1.3550; n_D^{20} 1.5413. It did not react with water at room temperature, but remained as an oil at the bottom of the flask. The literature [2] gives 80-82° b.p. 50 mm; d_0^{20} 1.36.

Found %: S 20.19; 20.06

$C_2H_5PSCl_2$. Calculated %: S 19.63.

6. Synthesis of Diethyl Ethylphosphonothionate via the Phosphonothionic Chloride. The ester was prepared from the phosphonothionic chloride (30 g), alcohol (17 g), and pyridine (29 g) in xylene; it was prepared also in alcoholic solution by the action of the alkoxide. The reaction was carried out in both cases in a three-necked flask fitted with stirrer and reflux condenser. The first method is the less satisfactory, for it yields an ester that has an unpleasant smell, even after it has been washed with water; also, a higher temperature is required. The ester obtained has a slightly acid character, which is not found when the ester is prepared by the action of the alkoxide or by addition of sulfur to diethyl ethylphosphonite.

7. Synthesis of Diethyl Ethylphosphonoselenonate. Diethyl ethylphosphonite (15 g) and "metallic" selenium (7.9 g) were introduced into a round-bottomed flask fitted with stirrer and reflux condenser. The selenium

added rapidly, and the temperature rose from 19° to 85°. The product was vacuum-distilled, yielding a product (17 g, 75%) of b.p. 97.5°/11.5 mm, d_0^{20} 1.2743; n_D^2 1.4872.

Found %: Se 34.20; 33.82

$C_6H_{15}O_2PSe$. Calculated %: Se 37.49

Diethyl ethylphosphonoselenonate is a colorless liquid having a feeble but characteristic odor.

8. Synthesis of Diethylphosphinic Chloride. A solution of ethyl diethylphosphinate (27 g) in carbon tetrachloride (54 g) was placed in a three-necked flask fitted with stirrer, reflux condenser, and thermometer. Phosphorus pentachloride was added slowly to the ester at 30°; toward the end, the temperature was raised to 60°. The solvent and the phosphoryl chloride formed were driven off under somewhat reduced pressure, and the acid chloride was then distilled over (17 g, 70%); it had b.p. 108-109.5/16 mm, d_0^{20} 1.1394; n_D^{20} 1.4647; found MR_D 34.07; calculated MR_D 33.59.

Found %: Cl 25.40; 25.54

$C_4H_{10}OPCl$. Calculated %: Cl 25.27

9. Synthesis of Isobutylphosphonous Dichloride. No description of isobutylphosphonous dichloride has appeared in the literature. We synthesized it from magnesium (18.22 g), cadmium iodide (110 g), isobutyl bromide (113 g), and phosphorus trichloride (130 g). The yield of analytically pure substance was 30 g (26%). It is a colorless liquid having a characteristic odor that is less powerful than that of the ethyl homolog. It has b.p. 48.5-49° or 12 mm; d_0^{20} 1.172; n_D^{20} 1.4719; found MR_D 38.54; calculated MR_D 38.15.

Found %: Cl 43.75; 43.52

$C_4H_9PCl_2$. Calculated %: Cl 44.20

10. Synthesis of Diisobutyl Isobutylphosphonite. Isobutyl alcohol (28 g) and pyridine (30 g) were dissolved in dry ether and introduced into a round-bottomed three-necked flask fitted with reflux condenser and stirrer. Slight cooling was applied, and isobutylphosphonous dichloride (30 g) was added gradually. The pyridine hydrochloride formed was filtered off, and the ether was driven off. The residue was vacuum-distilled, yielding a colorless liquid (36 g, 85%) having a characteristic odor, reminiscent of that of phosphorous esters. It had b.p. 105.5-107.5° at 12.5 mm, d_0^{20} 0.8677; n_D^{20} 1.4290; found MR_D 69.20; calculated MR_D 69.60.

Found %: P 13.24; 13.38

$C_{12}H_{27}PO_2$. Calculated %: P 13.28

11. Addition of Bromine to Diisobutyl Isobutylphosphonite. The ester (1.021 g) was placed in a test tube cooled to -15°; carbon dioxide was passed into it continuously in order to avoid reaction with oxygen. Bromine was added slowly until the liquid remained slightly yellow in color; 0.7 g was required (0.7 g is the calculated amount). The addition went quantitatively with evolution of much heat.

12. Addition of Cuprous Bromide to Diisobutyl Isobutylphosphonite. Cuprous bromide (0.57 g) was added to the ester (0.94 g), and the temperature rose from 17° to 60°. A colorless syrup was formed, and it was not found possible to isolate a crystalline product.

13. Synthesis of Diisobutyl Isobutylphosphonothionate. The ester was prepared by addition of sulfur to diisobutyl isobutylphosphonite. The latter (5 g) was dissolved in dry benzene in a flask fitted with reflux condenser, and the calculated amount of sulfur was added. The temperature rose from 18° to 90°. Benzene was driven off, and the residue was vacuum-distilled. The yield was quantitative. The ester is a colorless liquid of a pleasant but feeble odor. It has b.p. 135-136.5° or 12 mm; d_0^0 0.9865; d_0^{20} 0.9636; n_D^{20} 1.4480.

Found %: S 11.90, 11.84

$C_{12}H_{27}O_2PS$. Calculated %: S 12.0

Some (3 g) of the ester was hydrolyzed by boiling it with concentrated hydrochloric acid in a flask fitted with reflux condenser. The acid obtained is a paraffin-like substance, and its study is not yet complete.

14. Synthesis of Diisobutyl Isobutylphosphonoselenonate. Diisobutyl isobutylphosphonite (9 g) was introduced into a flask fitted with reflux condenser. Powdered "metallic" selenium (3 g) was added (in absence of solvent), and the temperature rose from 18° to almost 80°. The product was heated further on the water bath for one hour and was then vacuum-distilled, yielding a colorless liquid (11 g, i.e., higher than 90%) of characteristic odor having b.p. 144-146° at 14 mm; d_0^{20} 1.084; n_D^{20} 1.4571. Yield 11 g (about 90% of theory).

Found %: Se 24.80; 24.90

$C_{12}H_{27}O_2PSe$. Calculated %: Se 25.20

15. Synthesis of Isobutyl Diisobutylphosphinate. A mixture of diisobutyl isobutylphosphonite (12 g) and isobutyl iodide (9 g) was heated in a sealed tube for three hours at 100°, heating being interrupted every hour in order to enable any change in the volume of the liquid to be noted. After three hours the volume of the contents of the tube did not change further. The product was vacuum-distilled yielding a colorless liquid (9.5 g, 80%) having a faint characteristic odor. The ester is insoluble in water, but soluble in ether. It has b.p. 99-102° at 2 mm; d_0^{21} 0.9151; n_D^{21} 1.4311; found MR_D 66.21; calculated MR_D 66.47.

Found %: P 13.41; 13.25

$C_{12}H_{27}PO_2$. Calculated %: P 13.28.

Some (4.5 g) of the ester obtained was hydrolyzed with concentrated hydrochloric acid in a sealed tube at 150-160° for three hours. When the tube was opened, there was an odor of isobutene. Hydrogen chloride was evaporated off in a dish, and the acid remained as a paraffinlike substance, which was not investigated further. Hofmann [5], who obtained the same acid by oxidation of the phosphine, described it as a liquid, insoluble in water.

SUMMARY

1. Certain alkylphosphonous esters have been synthesized.

2. Their ability to combine with halogen, sulfur, and selenium and to undergo oxidation has been demonstrated.

3. The ability of ethylphosphonous dichloride to unite readily with sulfur in presence of a catalyst has been demonstrated.

4. The greater ease with which the esters $RP(OR)_2$, as compared with the esters $P(OR)_3$ and $ArP(OR)_2$, undergo addition and isomerization reactions has been demonstrated, and an explanation has been given for this phenomenon.

5. Esters of dialkylphosphinic and alkylphosphonoselonic acids have been synthesized for the first time.

6. Methods have been given for the synthesis of alkylphosphonothionic acids.

LITERATURE CITED

[1] A. E. Arbuzov, "Catalysis Phenomena in the Reactions of Certain Phosphorus Compounds", Kazan, 1914.

[2] R. B. Fox, J. Am. Chem. Soc. 72, 4147 (1950).

[3] M. Kharasch, E. Jensen, S. Weinhause, J. Org. Chem. 14, 429, (1951).

[4] F. Guichard, Ber. 32, 1572 (1899).

[5] A. Hofmann, Ber. 4, 605 (1871).

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NEW METHOD FOR THE SYNTHESIS OF PHOSPHONIC AND PHOSPHINIC ESTERS AND THEIR THIO ANALOGS

COMMUNICATION 15. ADDITION OF PHENYL- AND ALKYL-PHOSPHONOUS ESTERS TO METHACRYLIC AND ACRYLIC ESTERS

A. N. Pudovik and D. Kh. Yarmukhametova

Esters of carboxy phosphonic (dihydroxyphosphinyl carboxylic) acids, as one of us has shown [1], may be readily prepared by the new method that we have developed for their synthesis: addition of dialkylphosphorous acids to α,β-unsaturated carboxylic esters. The reactions go very readily, in presence of a small amount of sodium alkoxide, and much heat is evolved; esters of carboxy phosphonic acids are obtained generally in high yield. Addition reactions have been carried out with equal success between dialkylphosphorous acids and esters of unsaturated dibasic acids: maleic, fumaric, and acetylenedicarboxylic. In the last case addition products were obtained which were formed by addition of two dialkylphosphorous acid molecules at the triple bond: esters of 1,2-dicarboxyethylenediphosphonic [α,β-bis(dihydroxyphosphinyl)succinic] acid.

We decided to study, as a development and extension of our previous work, the addition of partial esters of aryl- and alkyl-phosphonous acids to esters of unsaturated carboxylic acids. In this investigation we have chosen for study the addition of partial phenylphosphonous esters and of butyl hydrogen ethylphosphonite. It should be noted that aryl- and alkyl-phosphonous esters have received very little study. Only the butyl ester of phenylphosphonous acid is described [2] in the literature, and esters of alkylphosphonous acids were recently synthesized for the first time by B. A. Arbuzov and Rizpolozhensky [3], working in our laboratory. We have synthesized various esters of phenylphosphonous acid by the action of the corresponding alcohols on phenylphosphonous dichloride:

$$C_6H_5PCl_2 + 2ROH \longrightarrow C_6H_5P(OR)(OR) + 2HCl \longrightarrow C_6H_5P(OR)(OH) + RCl + HCl.$$

Constants and yields of the substances obtained are given in Table 1.

It should be noted that ethyl hydrogen phenylphosphonite, in spite of the contrary findings of Kosolapoff, was very readily prepared in good yield and had a characteristic odor, similar to that of other members of the series. We therefore found it quite possible to characterize it as a pure, individual substance and to apply it in synthesis. In our examination of the series of partial phenylphosphonous esters that we have prepared we gave some consideration to the rather considerable discrepancy between the calculated and determined values of the molecular refraction. In all cases the determined molecular refraction exceeded the calculated value by 1.1-1.5, which can evidently be explained by the constitutive effect of the phenyl group on the atomic refraction of phosphorus.

The addition of partial esters of phenylphosphonous acid to methacrylic and acrylic esters was effected by us by the usual procedure, which is described in detail in previous papers [4]. The reactions were very vigorous, and much heat was evolved. A solution of sodium ethoxide in absolute ethanol was used as catalyst: no exchange of radicals between alcohol and ester was observed, products of sharp boiling point being obtained in all cases, without any detectable by-products. The reactions went according to the equation:

$$C_6H_5P(OR')(OH) + CH_2 = CR''-COOR''' \xrightarrow{C_2H_5ONa} C_6H_5P(OR')(=O)-CH_2-CHR''-COOR''',$$

where $R' = C_2H_5, C_4H_9, C_6H_{13}$, $R'' = H$ or CH_3; $R''' = CH_3, C_2H_5, C_3H_7$.

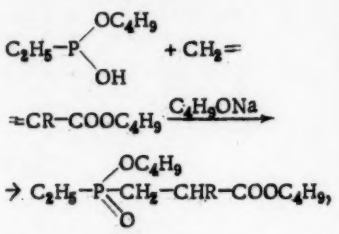
TABLE 1

No.	Formula	B.p. (°C/1 mm)	n_D^{20}	d_4^{20}	Yield (%)
1	$C_6H_5(CH_3O)POH$	91-93	1.5322	1.1770	66
2	$C_6H_5(C_2H_5O)POH$	94-95	1.5231	1.1291	84
3	$C_6H_5(i\text{-}C_3H_7O)POH$	106-107	1.5111	1.0922	70
4	$C_6H_5(i\text{-}C_4H_9O)POH$	112-113	1.5081	1.0675	88
5	$C_6H_5(n\text{-}C_6H_{13}O)POH$	139	1.5030	1.0388	60
6	$C_6H_5(n\text{-}C_7H_{15}O)POH$	150	1.4996	1.0187	80
7	$C_6H_5(n\text{-}C_8H_{17}O)POH$	155	1,4982	1.0079	78
8	$C_6H_5(n\text{-}C_9H_{19}O)POH$	158-160	1.4900	0.9843	57

TABLE 2

No.	Formula	B.p. (°C)	Pressure (mm Hg)	n_D^{20}	d_4^{20}	Yield (%)
1	$C_6H_5(C_2H_5O)P(=O)CH_2CH(CH_3)COOCH_3$	141-143	0.5	1.5064	1.1390	72
2	$C_6H_5(C_2H_5O)P(=O)CH_2CH_2COOCH_3$	159-160	2	1.5081	1.1619	76
3	$C_6H_5(C_2H_5O)P(=O)CH_2CH(CH_3)COOC_2H_5$	159-160	1	1.4992	1.1140	82
4	$C_6H_5(C_2H_5O)P(=O)CH_2CH(CH_3)COOC_3H_7$	149	0.6	1.4962	1.0988	74
5	$C_6H_5(i\text{-}C_4H_9O)P(=O)CH_2CH(CH_3)COOCH_3$	156	1	1.4965	1.0962	45
6	$C_6H_5(C_6H_{13}O)P(=O)CH_2CH(CH_3)COOCH_3$	176-177	1	1.4908	1.0589	40
7	$C_2H_5(C_4H_9O)P(=O)CH_2CH(CH_3)COOC_4H_9$	137-138	1	1.4490	1.0025	75
8	$C_2H_5(C_4H_9O)P(=O)CH_2CH_2COOC_4H_9$	141	1	1.4490	1.0146	74

When reactions were carried out under similar conditions between partial esters of alkylphosphonous acids and various esters of acrylic and methacrylic acids, we were unable to obtain completely pure products. Most of them had a wide boiling range (3-5°), and besides the main product appreciable amounts of lower- and higher-boiling fractions were obtained. Since the contamination of the main reaction product could arise from secondary products formed as a result of radical exchange between ester and alcohol groups, we carried out experiments in which the radicals of the ester groups and of the alcohol used for preparation of alkoxide were identical. We then obtained addition products having sharp boiling points: their phosphorus contents corresponded accurately to the calculated values. The reaction was as follows:



where R = H or CH_3.

Constants and yields of addition products formed by partial phenyl- and ethylphosphonous esters with acrylic and methacrylic esters are given in Table 2.

EXPERIMENTAL

Prepration of Alkyl Hydrogen Phenylphosphonites.

Methyl hydrogen phenylphosphonite. Phenylphosphonous dichloride (14.6 g) was added dropwise

to absolute methanol (15 g) contained in an Arbuzov flask. Hydrogen chloride was drawn off over a period of 3-4 hours, and the reaction mixture was then vacuum-fractionated, yielding methyl hydrogen phenylphosphonite (8.4 g).

Found %: P 19.89; 20.23
$C_7H_9O_2P$. Calculated %: P 19.87

Ethyl hydrogen phenylphosphonite. The procedure was similar to that of the previous experiment. Phenylphosphonous dichloride (25 g) and absolute ethanol (20 g) yielded ethyl hydrogen phenylphosphonite (20 g).

Found %: P 18.11; 17.92
$C_8H_{11}O_2P$. Calculated %: P 18.23

Isopropyl hydrogen phenylphosphonite. Phenylphosphonous dichloride (11.3 g) and absolute isopropyl alcohol (11.3 g) yielded isopropyl hydrogen phenylphosphonite (9.3 g).

Found %: P 16.86; 16.67
$C_9H_{13}O_2P$. Calculated %: P 16.85

Isobutyl hydrogen phenylphosphonite. Phenylphosphonous dichloride (14.8 g) and absolute isobutyl alcohol (18.5 g) yielded isobutyl hydrogen phenylphosphonite (14.4 g).

Found %: P 15.79
$C_{10}H_{15}O_2P$. Calculated %: P 15.66

Hexyl hydrogen phenylphosphonite. Phenylphosphonous dichloride (10.7 g) and dry hexyl alcohol (18.3 g) yielded hexyl hydrogen phenylphosphonite (8 g):

Found %: P 13.72
$C_{12}H_{19}O_2P$. Calculated %: P 13.48

Heptyl hydrogen phenylphosphonite. Phenylphosphonous dichloride (10 g) and heptyl alcohol (19 g) yielded heptyl hydrogen phenyl-phosphonite (10.7 g).

Found %: P 12.82; 12.18
$C_{13}H_{21}O_2P$. Calculated %: P 12.92

Octyl hydrogen phenylphosphonite. Phenylphosphonous dichloride (8.8 g) and octyl alcohol (19.2 g) yielded octyl hydrogen phenylphosphonite (9.6 g).

Found %: P 12.32
$C_{14}H_{23}O_2P$. Calculated %: P 12.20

Nonyl hydrogen phenylphosphonite. Phenylphosphonous dichloride (10 g) and nonyl alcohol (24 g) yielded nonyl hydrogen phenylphosphonite (8.5 g).

Found %: P 11.33
$C_{15}H_{25}O_2P$. Calculated %: P 11.57

Addition of Ethyl Hydrogen Phenylphosphonite to Methyl Methacrylate

The reaction was carried out in an Arbuzov flask. A saturated solution of sodium ethoxide (4-5 drops) was added to a mixture of ethyl hydrogen phenylphosphonite (7 g) and methyl methacrylate (4.1 g), and reaction proceeded with evolution of much heat. The reaction mixture was vacuum-distilled yielding ethyl (2-methoxycarbonylpropyl)phenyl phosphinate (8 g) having b.p. 141-143° at 0.5 mm; n_D^{20} 1.5064; d_4^{20} 1.1390.

Found %: P 11.78
$C_{13}H_{19}O_4P$. Calculated %: P 11.48

Addition of Ethyl Hydrogen Phenylphosphonite to Methyl Acrylate

The procedure was similar to that of the previous experiment. Ethyl hydrogen phenylphosphonite (5 g) and methyl acrylate (2.5 g) yielded ethyl (2-methoxycarbonylethyl)phenylphosphinate (5.7 g) having b.p. 159-160° at 2 mm; n_D^{20} 1.5081; d_4^{20} 1.1619.

Found %: P 12.46; 12.36
$C_{12}H_{17}O_4P$. Calculated %: P 12.11

Addition of Ethyl Hydrogen Phenylphosphonite to Ethyl Methacrylate

Ethyl hydrogen phenylphosphonite (3 g) and ethyl methacrylate (2 g) yielded ethyl (2-ethoxycarbonylpropyl) phenylphosphinate (4.1 g) having b.p. 159-160°at 1 mm; n_D^{20} 1.4992; d_4^{20} 1.1140

Found %: P 11.12; 11.07

$C_{14}H_{21}O_4P$. Calculated %: P 10.92

Addition of Ethyl Hydrogen Phenylphosphonite to Propyl Methacrylate

Ethyl hydrogen phenylphosphonite (3 g) and propyl methacrylate (2.3 g) yielded ethyl (2-propoxycarbonylpropyl)phenylphosphinate (4 g) having b.p. 149° at 1 mm; n_D^{20} 1.4962; d_4^{20} 1.0988.

Found %: P 10.35; 10.67

$C_{15}H_{23}O_4P$. Calculated %: P 10.40

Addition of Isobutyl Hydrogen Phenylphosphonite to Methyl Methacrylate

Isobutyl hydrogen phenylphosphonite (6.1 g) and methyl methacrylate (3 g) yielded isobutyl (2-methoxycarbonylpropyl)phenylphosphinate (4 g) having b.p. 156° or 1 mm; n_D^{20} 1.4965; d_4^{20} 1.0962

Found %: P 10.50; 10.47

$C_{15}H_{23}O_4P$. Calculated %: P 10.40

Addition of Hexyl Hydrogen Phenylphosphonite to Methyl Methacrylate

Hexyl hydrogen phenylphosphonite (4 g) and methyl methacrylate (1.8 g) yielded hexyl (2-methoxycarbonylpropyl)phenylphosphinate (2.3 g) having b.p. 176-177° at 1 mm; n_D^{20} 1.4908; d_4^{20} 1.0589.

Found %: P 9.25; 9.28

$C_{17}H_{27}O_4P$. Calculated %: P 9.20

Addition of Butyl Hydrogen Ethylphosphonite to Butyl Methacrylate

Butyl hydrogen ethylphosphonite (4 g) and butyl methacrylate (3.8 g) yielded butyl (2-butoxycarbonylpropyl) ethylphosphinate (5.9 g) having b.p. 137-138° at 1 mm; n_D^{20} 1.4490; d_4^{20} 1.0025.

Found %: P 10.89

$C_{14}H_{29}O_4P$. Calculated %: P 10.62

Addition of Butyl Hydrogen Ethylphosphonite to Butyl Acrylate

Butyl hydrogen ethylphosphonite (4 g) and butyl acrylate (3.4 g) yielded butyl (2-butoxycarbonylethyl)ethylphosphinate (5.5 g) having b.p. 141° at 1 mm; n_D^{20} 1.4490; d_4^{20} 1.0146.

Found %: P 11.12; 11.12

$C_{13}H_{27}O_4P$. Calculated %: P 11.15

SUMMARY

1. The methyl, ethyl, isopropyl, isobutyl, hexyl, heptyl, octyl, and nonyl partial esters of phenylphosphonous acid have been synthesized.

2. It has been shown that, in presence of alkali-metal alkoxides, partial esters of phenylphosphonous and alkylphosphonous acids readily add on to methacrylic and acrylic esters.

3. Various esters of (2-alkoxycarbonylethyl)phenyl-, (2-alkoxycarbonylethyl)ethyl-, (2-alkoxycarbonylpropyl)phenyl-, and (2-alkoxycarbonylpropyl)ethyl-phosphinic acids have been synthesized.

LITERATURE CITED

[1] A.N. Pudovik, J. Gen. Chem., 22, 467, (1952)* [2] G. Kosolapoff, J. Am. Chem. Soc. 72, 4292 (1950). [3] B.A. Arbuzov and N.I. Rizpolozhensky, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., No. 5, 956, (1952)** [4] A. N. Pudovik, Proc. Acad. Sci. U.S.S.R., 73, 499 (1950).

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* See Consultants Bureau translation, p 537.

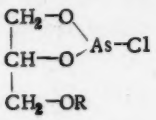
** See Consultants Bureau translation, p. 843.

PREPARATION OF CYCLIC ACID CHLORIDES AND MIXED ESTERS DERIVED FROM (ALKOXYMETHYL)ETHYLENE HYDROGEN ARSENITES AND TRIMETHYLENE HYDROGEN ARSENITE

Gilm Kamai and N. A. Chadaeva

Acid chlorides derived from arsenious acid have received very little study in comparison with that received by acid chlorides derived from phosphorous acid. This situation probably arises from the difficulty with which the arsenic compounds are prepared and from their instability. Ethyl arsenodichloridite and diethyl arsenochloridite were prepared for the first time in 1920 by McKenzie and Wood [1] by the action of arsenic trichloride on sodium ethoxide. In 1951 Kamai and Khisamova [2] described the preparation and properties of the first cyclic acid chloride and of certain alkyl (and cycloalkyl) ethylene arsenites.

The object of the present investigation was the preparation of further cyclic acid chlorides and mixed esters, derived, in this case, from (alkoxymethyl)ethylene hydrogen arsenites and from trimethylene hydrogen arsenite. As a result of our experiments we have synthesized the following acid chlorides (arsenochloridites):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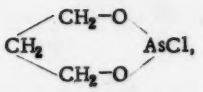
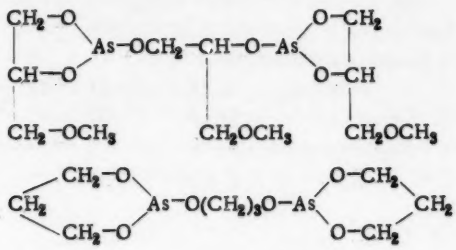
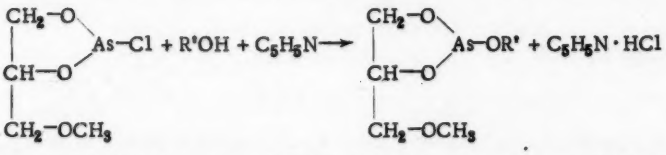


where R = CH_3, C_2H_5, i-C_3H_7, and n-C_4H_9.

In the synthesis of certain cyclic arsenochloridites in dry ether in presence of pyridine, we isolated the following full cyclic esters from the high-boiling fractions:



When these esters were heated with arsenic trichloride (equimolecular quantities), they were completely converted into the corresponding arsenochloridites. Also, by the reaction of (methoxymethyl)ethylene arsenochloridite with anhydrous alcohols in a medium of ether and pyridine, we have prepared various mixed esters:



By this method methyl, ethyl, propyl, butyl, hexyl, cyclohexyl, and phenyl (methoxymethyl)ethylene arsenites were prepared. These esters are colorless oils, readily miscible with many organic solvents and smelling, in some cases, rather like the original alcohols. They are hydrolyzed by water, giving arsenious oxide, 3-methoxy-1,2-propanediol, and the corresponding alcohols.

EXPERIMENTAL

Preparation of (Methoxymethyl)ethylene Arsenochloridite

Reaction carried out in absolute ether. A mixture of 3-methoxy-1,2-propanediol (32 g), freshly distilled

pyridine (47.5 g) and about 400 ml absolute diethyl ether was introduced into a round-bottomed flask fitted with a mechanical stirrer, reflux condenser, and dropping funnel. The mixture was cooled to −5° and was stirred while 54.5 g arsenic trichloride was added from the dropping funnel. When about one-third of the total amount of arsenic trichloride had been added, a crystalline precipitate began to form. As soon as the calculated amount of arsenic trichloride had been added, cooling was discontinued, and the reaction mixture was heated on a water bath for one hour. It was allowed to stand overnight, and next day the ethereal solution was removed from the precipitate by decantation and the precipitate was washed three times with absolute ether. The solvent was driven off, and the residual liquid was vacuum-distilled, yielding the following two fractions:

Fraction I, b.p. 98-105°/10 mm; 43 g

Fraction II, b.p. 184-200°/3 mm; 8 g

In a second fractionation of Fraction I a cut of b.p. 102-104°/10 mm was taken.

Found %: As 35.25, 35.14; Cl 16.75

$C_4H_8O_3AsCl$. Calculated %: As 34.94; Cl 16.54

The product obtained was (methoxymethyl) ethylene arsenochloridite with the constants: d_0^0 1.7043; d_0^{20} 1.6771; n_D^{20} 1.5330; found MR_D 39.69; calculated for $C_4H_8O_3AsCl$ MR_D 39.45.

This arsenochloridite is a colorless liquid, soluble in ether, benzene, alcohol, carbon tetrachloride, and other organic solvents.

Fraction II also was fractionated further, yielding a product (1.7 g) of b.p. 197-200°/3 mm.

Found %: As 32.02, 32.52

$C_{12}H_{24}O_9As_2$. Calculated %: As 32.12

This substance is the full (methoxymethyl) ethylene ester of arsenious acid having the formula already cited; it has d_0^{20} 1.5762; d_0^{20} 1.5545; n_D^{20} 1.5095; found MR_D 86.26; calculated for $C_{12}H_{24}O_9As_2$ MR_D 86.63. It is a thick oil of good solubility in organic solvents.

Reaction in absence of solvent. Arsenic trichloride (55 g), contained in a flask, was heated to boiling, and 31 g 3-methoxy-1,2-propanediol was added from a dropping funnel. When the addition was complete, the reaction mixture was heated until evolution of hydrogen chloride ceased. The reaction mixture was then transferred to a distillation flask and was vacuum-distilled, yielding the following fractions:

Fraction I, b.p. 68-100°/11 mm; 18 g

Fraction II, b.p. 100-105°/11 mm; 45 g

Residue 3 g

Fraction II was analyzed without a second distillation:

Found %: As 34.16,34.17; Cl 17.13

$C_4H_8O_3AsCl$. Calculated %: As 34.94; Cl 16.54

According to the analytical data the substance was (methoxymethyl) ethylene arsenochloridite: d_0^0 1.7185; d_0^{20} 1.6880; n_D^{20} 1.5313; found MR_D 40.04; calculated for $C_4H_8O_3AsCl$ MR_D 39.45.

Hydrolysis of (Methoxymethyl) ethylene Arsenochloridite

A mixture of 3 g of (methoxy) ethylene arsenochloridite and 50 ml water was heated for one hour and then left overnight. The white precipitate that separated was filtered off, washed several times with water, dried to constant weight, and analyzed:

Found %: As 73.34, 73.35

As_2O_3. Calculated %: As 75.73

The white precipitate was therefore impure arsenious oxide.

Preparation of (Ethoxymethyl)ethylene Arsenochloridite

3-Ethoxy-1,2-propanediol (30 g) was added from a dropping funnel to 46.0 g boiling arsenic trichloride. After being heated for two hours, the reaction mixture was vacuum-fractionated:

Fraction I, b.p. 57-102°/13-10 mm; 5 g

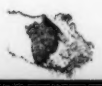
Fraction II, b.p.102-113°/10 mm; 51 g

Residue 1.5 g

A second fractionation of Fraction II yielded 40 g of a product of b.p. 105.5-107°/9 mm.

Found %: As 32.99, 33.11; Cl 15.64,15.59

$C_5H_{10}O_3AsCl$. Calculated %: As 32.8; Cl 15.5



(Ethoxymethyl)ethylene arsenochloridite is a colorless liquid, soluble in many organic solvents; it has the constants: d_0^0 1.6132; d_0^{20} 1.5847; n_D^{20} 1.5160; found MR_D 43.55; calculated for $C_5H_{10}O_3AsCl$ MR_D 43.89.

Preparation of (Isopropoxymethyl)ethylene Arsenochloridite

Reaction of 41 g arsenic trichloride with 22 g 3-isopropoxy-1,2-propanediol yielded, by the method described for the previous arsenochloridites, 46 g of a substance of b.p. 110-117°/10 mm. A second distillation of this fraction yielded 35.6 g of a product of b.p. 114-116°/9 mm.

Found %: As 30.76, 30.84; Cl 14.15; 14.24

$C_6H_{12}O_3AsCl$. Calculated %: As 30.89; Cl 14.62

(Isopropoxymethyl)ethylene arsenochloridite is similar in properties to the arsenochloridites described above: d_0^0 1.5335; d_0^{20} 1.5060; n_D^{20} 1.5061; found MR_D 47.83; calculated for $C_6H_{12}O_3$ AsCl MR_D 48.59.

Preparation of (Butoxymethyl)ethylene Arsenochloridite

Reaction of arsenic trichloride (62 g) with 50 g 3-butoxy-1,2-propanediol (cf. preceding syntheses) yielded 60 g of a product with b.p. 129-130°/9 mm; d_0^0 1.4619; d_0^{20} 1.4273; n_D^{20} 1.5019; found MR_D 53.05; calculated for $C_7H_{14}O_3AsCl$ MR_D 53.11.

Found %: As 29.34, 29.22; Cl 13.89, 13.85

$C_7H_{14}O_3AsCl$. Calculated %: As 29.13; Cl 13.82

The arsenochloridite is a colorless, odorless liquid, soluble in organic solvents. It is readily hydrolyzed by water.

Preparation of (Chloromethyl)ethylene Arsenochloridite

Reaction of 37 g arsenic trichloride and 22 g 3-chloro-1,2-propanediol (cf. previous syntheses) yielded 18 g of a substance of b.p. 103-105°/11 mm.

Found %: As 33.95, 33.46; Cl 32.10

$C_2H_5O_2Cl_2As$. Calculated %: As 34.21; Cl 32.37

(Chloromethyl)ethylene arsenochloridite is a thick odorless liquid having d_0^0 1.9446; d_0^{20} 1.9131; n_D^{20} 1.5664; found MR_D 37.38; calculated for $C_3H_5O_2Cl_2As$ MR_D 38.2

Preparation of Trimethylene Arsenochloridite

Arsenic trichloride (80 g) was added to 30 g stirred cooled (−5°) mixture of 1,3-propanediol, 62.5 g freshly distilled pyridine, and 400 ml absolute diethyl ether. When the whole of the arsenic trichloride had been added, the reaction mixture was heated on a water bath for one hour and then allowed to stand overnight. Next day the ethereal solution was decanted from the crystalline precipitate, and the precipitate was washed three times with absolute ether. The solvent was driven off, and the residual liquid was vacuum-distilled. The following fractions were obtained:

Fraction I, b.p. 30-65°/10 mm; 10 g
Fraction II, b.p. 65-71°/10 mm; 34 g
Fraction III, b.p. 124-180°/2 mm; 16.5 g

A second fractionation of Fraction II yielded 21 g of a product of b.p. 66-67°/10 mm.

Found %: As 39.99, 40.29; Cl 19.04, 18.90

$C_3H_6O_2AsCl$. Calculated %: As 40.57; Cl 19.22

This product is trimethylene arsenochloridite and has the constants: d_0^0 1.7938; d_0^{20} 1.7624; n_D^{20} 1.5418; found MR_D 32.95; calculated for $C_3H_6O_2AsCl$ MR_D 33.19.

Fraction III was also refractionated and yielded 4.2 g of a product of b.p. 164-167°/3 mm.

Found %: As 40.10

$C_9H_{18}O_6As_2$. Calculated %: As 40.21

The full trimethylene ester of arsenious acid is a very thick, clear, odorless liquid. It has d_0^0 1.8213; d_0^{20} 1.7954; n_D^{20} 1.5139.

Preparation of (Methoxymethyl)ethylene Methyl Arsenite

Sodium (3.54 g) was added under stirring to 50 ml methanol contained in a round-bottomed flask. The solution of methoxide was cooled to 0°, and 32.2 g (methoxymethyl)ethylene arsenochloridite was added from a dropping funnel. The first drops of the arsenochloridite caused the solution to become turbid. When the calculated amount had been added, the reaction mixture was heated on a water bath for one hour, and was then allowed to stand overnight. The sodium chloride formed was filtered off through a fine sintered-glass filter, and was washed twice with

dry methanol. The solvent was driven off, and the residual liquid was vacuum-fractionated, yielding the fractions:

Fraction I, b.p. 39-90°/13 mm

Fraction II, b.p. 90-93°/13 mm

Fraction III, b.p. 200-218°/3-4 mm

Redistillation of Fraction II yielded 6 g of a product of b.p. 91-92°/11 mm.

Found %: As 35.46, 35.08

$C_5H_{11}O_4As$. Calculated %: As 35.66

(Methoxymethyl)ethylene methyl arsenite is a mobile, colorless liquid having a specific odor. It is readily soluble in ether, alcohols, benzene, and other organic solvents. It is rapidly hydrolyzed by water. It has d_0^0 1.5311; d_0^{20} 1.5044; n_D^{20} 1.4798; found MR_D 39.77; calculated for $C_5H_{11}O_4As$: MR_D 40.28.

Preparation of Ethyl (Methoxymethyl)ethylene Arsenite

(Methoxymethyl)ethylene arsenochloridite (21.5 g) was added to a cooled (0°) mixture of 4.6 g of dry ethanol, 7.9 g distilled pyridine, and 200 ml absolute diethyl ether. Toward the end of the addition, cooling was discontinued. When the calculated amount of the arsenochloridite had been added, the reaction mixture was heated on a water bath for one hour. On the next day the precipitate of pyridine hydrochloride was separated by decantation of the solution, and was washed several times with small amounts of dry ether. The solvent was distilled off, and the residual liquid was vacuum-fractionated, yielding the three fractions:

Fraction I, b.p. 58-87°/11 mm; 3 g

Fraction II, b.p. 88-103°/11 mm; 8.5 g

Fraction III, b.p. 168-185°/3 mm; 8.9 g

Redistillation of Fraction II yielded 3.9 g of a substance of b.p. 97-98°/10 mm.

Found %: As 33.23, 33.66

$C_6H_{13}O_4As$. Calculated %: As 33.43

Ethyl (methoxymethyl)ethylene arsenite is a clear, mobile liquid, readily hydrolyzed in damp air with formation of arsenious oxide. It has d_0^0 1.4378; d_0^{20} 1.4172; n_D^{20} 1.4788; found MR_D 44.82; calculated for $C_6H_{13}O_4As$ MR_D 44.79.

Preparation of (Methoxymethyl)ethylene Propyl Arsenite

(Methoxymethyl)ethylene arsenochloridite (33.0 g) was added to a stirred, cooled (0°) mixture of 9 g propyl alcohol, 11.4 g freshly distilled pyridine, and 200 ml absolute diethyl ether. After removal of pyridine hydrochloride and of solvent, the residual liquid was vacuum-fractionated:

Fraction I, b.p. 100-104°/12 mm

Fraction II, b.p. 104.5-106°/12 mm; 22.5 g

Fraction III, b.p. 116-167°/3 mm

Three further fractionations of Fraction II resulted in the isolation of 10 g of a product having b.p. 101-103°/12 mm.

Found %: As 32.26, 32.56; Cl 1.83

$C_7H_{15}O_4As$. Calculated %: As 31.46

This preparation of (methoxymethyl)ethylene propyl arsenite was not completely pure: it was contaminated with the original arsenochloridite, whose boiling point is very close to that of the mixed ester. The product had the constants: d_0^{20} 1.3781; n_D^{20} 1.4762, found MR_D 48.47; calculated $C_7H_{15}O_4As$: MR_D 49.12.

Preparation of Butyl (Methoxymethyl)ethylene Arsenite

Starting with butyl alcohol (9 g), 10 g pyridine, 150 ml absolute diethyl ether, and 30 g (methoxymethyl)-ethylene arsenochloridite and proceeding as in the previous syntheses, we obtained 20 g of a product of b.p. 122-124°/12 mm.

Found %: As 29.8, 29.47

$C_8H_{17}O_4As$. Calculated %: As 29.71.

Butyl (methoxymethyl)ethylene arsenite, like its analogs already described, is a colorless, mobile liquid having the specific odor of butyl alcohol. It has d_0^0 1.3481; d_0^{20} 1.3248; n_D^{20} 1.4731; found MR_D 53.39; calculated for $C_8H_{17}O_4As$: MR_D 54.14.

Preparation of Hexyl (Methoxymethyl)ethylene Arsenite

Starting with hexyl alcohol (11 g), 7.9 g pyridine, 200 ml absolute diethyl ether and 22 g (methoxymethyl)-ethylene arsenochloridite and proceeding as in the previous syntheses, we obtained 17 g of a product of b.p. 147-148°/11 mm, which was analyzed without redistillation:

Found %: As 27.01, 26.99

$C_{10}H_{27}O_4As$. Calculated %: As 26.73

Hexyl (methoxymethyl)ethylene arsenite is a liquid having a characteristic odor, reminiscent of the odor of hexyl alcohol. It is hydrolyzed by water. It has d_0^{20} 1.2618; d_0^{20} 1.2411; n_D^{20} 1.4703; found MR_D 63.05; calculated for $C_{10}H_{21}O_4As$; MR_D 63.38.

Preparation of Cyclohexyl (Methoxymethyl)ethylene Arsenite

Starting with 7.7 g cyclohexanol, 5.9 g pyridine, 200 ml absolute diethyl ether, and 16.3 g (methoxymethyl)ethylene arsenochloridite and proceeding as in the previous syntheses, we obtained, after a second distillation, 8 g of b.p. 140-142°/10 mm.

Found %: As 27.29, 27.3

$C_{10}H_{19}O_4As$. Calculated %: As 26.99

Cyclohexyl (methoxymethyl)ethylene arsenite is a clear oily liquid having d_0^0 1.3599; d_0^{20} 1.3376; n_D^{20} 1.4950; found MR_D 60.61; calculated for $C_{10}H_{19}O_4As$; MR_D 61.17.

Preparation of (Methoxymethyl)ethylene Phenyl Arsenite

Starting with freshly distilled phenol (19 g), dissolved in 400 ml absolute diethyl ether, 15.8 g pyridine, and 43 g (methoxymethyl)ethylene arsenochloridite and proceeding as in the previous syntheses, we obtained 12.2 g of a product of b.p. 162-163°/13 mm.

Found %: As 27.73, 27.58

$C_{10}H_{13}O_4As$. Calculated %: As 27.52

(Methoxymethyl)ethylene phenyl arsenite is a colorless, oily liquid having the characteristic odor of phenol. It is of good solubility in organic solvents. It is rapidly hydrolyzed by water. It has d_0^0 1.4787; d_0^{20} 1.4552; n_D^{20} 1.5520; found MR_D 59.52; calculated for $C_{10}H_{13}O_4As$; MR_D 61.30.

Reaction of the Full (Methoxymethyl)ethylene Ester of Arsenious Acid with Arsenic Trichloride

The full (methoxymethyl)ethylene ester of arsenious acid (12.8 g) was introduced into a round-bottomed flask provided with reflux condenser and dropping funnel. Arsenic trichloride (5.1 g) was added from the dropping funnel, addition being accompanied by shaking; heat was evolved. When the calculated amount of arsenic trichloride had been added, the reaction mixture was heated on an oil bath at 180-185° for 30 minutes. The mixture was then cooled and vacuum-fractionated, yielding:

Fraction I, b.p. 102-104°/12 mm

Fraction II, b.p. 105°/12 mm; 10.5 g

Fraction II was analyzed without being redistilled:

Found %: As 34.37; 34.03; Cl 16.27

$C_4H_8O_3AsCl$. Calculated %: As 34.94; Cl 16.54

The substance isolated was almost pure (methoxymethyl)ethylene arsenochloridite.

SUMMARY

1. A study has been made of new cyclic acid chlorides derived from (alkoxymethyl)ethylene hydrogen arsenites and from trimethylene hydrogen arsenite.

2. It has been found that, in the preparation of (methoxymethyl)ethylene arsenochloridite and of trimethylene arsenochloridite in a medium of ether and pyridine, full cyclic esters are formed at the same time.

3. Mixed arsenious esters containing the bivalent radical (methoxymethyl)ethylene have been investigated.

4. It has been shown that the arsenochloridites and mixed esters that have been synthesized are hydrolyzed by water with formation of arsenious oxide and of the corresponding glycols and alcohols.

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LITERATURE CITED

[1] McKenzie and Wood. J. Chem.Soc., 117, 406 (1920).

[2] Gilm Kamai and Z.L.Khisamova. Proc.Acad.Sci.USSR, 76, 535 (1951).

"PHOSPHONOETHYLATION" AND DIENE-SYNTHESIS REACTIONS WITH VINYLPHOSPHONIC ESTERS

A.N.Pudovik and M.G.Imaev

α,β-Unsaturated phosphonic esters form a very interesting, but at the same time very little studied class of organophosphorus compounds. There are only brief mentions in the literature, occurring mainly in patents [1], concerning the preparation of individual α,β-unsaturated phosphonic acids other than diethyl vinylphosphonate. The methods proposed, however, involve starting materials that are not readily available, give low yields, and are often of poor reproducibility. The method that has received most attention is that used for the synthesis of the simplest representative of compounds of this type, diethyl vinylphosphonate, which was prepared by Kabachnik [2] and by Kosolapoff [3] from diethyl 2-chloro- or 2-bromo-ethylphosphonate by the splitting off of a molecule of hydrogen halide. The properties of vinylphosphonic esters have, prior to our work, remained practically without study. In a series of previous investigations one of us has shown [4] that the vinylphosphonic esters form a very reactive group of unsaturated compounds, which, in particular, are capable of undergoing various addition reactions, in which they exhibit strongly pronounced electrophilic character. In presence of alkali–metal alkoxides we have brought about addition to diethyl vinylphosphonate of the following compounds: dialkylphosphorous acids; ammonia and amines; and malonic, cyanoacetic, and acetoacetic esters and their homologs. In the majority of cases we obtained diethyl esters of β-substituted ethylphosphonic acids in high yield. To this reaction we gave the name "phosphonoethylation", since it brings about the introduction of the phosphonoethyl, i.e. dihydroxyphosphinylethyl, radical into nucleophilic organic compounds of a large variety of types.

In the present work, our previous investigations are continued: we have further shown the possibility of the addition to vinylphosphonic esters of hydrogen sulfide and mercaptans, and also the possibility of using vinylphosphonic acids as dienophiles in diene-synthesis reactions. In addition to diethyl vinylphosphonate, we have used the dibutyl ester, synthesized by a modification of the method of Kabachnik and Kosolapoff. In carrying out the reaction between ethylene dibromide and tributyl phosphite, we obtained, as by-products, dibutyl butylphosphonate and tetrabutyl ethylenediphosphonate:

$$CH_2Br-CH_2Br + (C_4H_9O)_3P \longrightarrow BrCH_2-CH_2P(=O)(OC_4H_9)_2 + (C_4H_9O)_2P(=O)-CH_2-CH_2-P(=O)(OC_4H_9)_2 + C_4H_9P(=O)(OC_4H_9)_2 + C_4H_9Br.$$

$$Br-CH_2-CH_2-P(=O)(OC_4H_9)_2 + KOH \longrightarrow CH_2=CH-P(=O)(OC_4H_9)_2 + KBr + H_2O.$$

An attempt to prepare dimethyl vinylphosphonate was not successful: in the course of the reaction between ethylene dibromide and trimethyl phosphite, which was intended to yield dimethyl 2-bromoethylphosphonate, the trimethyl phosphite underwent rapid isomerization (owing to its high reactivity) under the influence of methyl bromide. The only reaction product was dimethyl methylphosphonate.

Addition of hydrogen sulfide and of ethanethiol to the diethyl and dibutyl esters of vinylphosphonic acid was carried out in absolute alcoholic solution in presence of sodium ethoxide. The reactions went readily even at room temperature; they proceeded more rapidly and with better yields at a higher temperature.

$$R-SH + C_2H_5ONa \rightleftharpoons RSNa + C_2H_5OH,\ R\bar{S}\overset{+}{Na} + \overset{+}{C}H_2=CH-P(=O^-)(OR')_2 \longrightarrow CH_2(SR)-CHNa-P(=O)(OR')_2$$

$$\text{or } CH_2(SR)-CH=P(ONa)(OR')_2 \xrightarrow{RSH} RS-CH_2-CH_2-P(=O)(OR')_2 + RSNa, \text{ etc.}$$

where R = H or C_2H_5, and R' = C_2H_5 or C_4H_9.

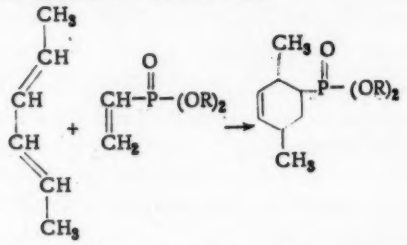
Constants and yields of the substances obtained are given in Table 1.

TABLE 1

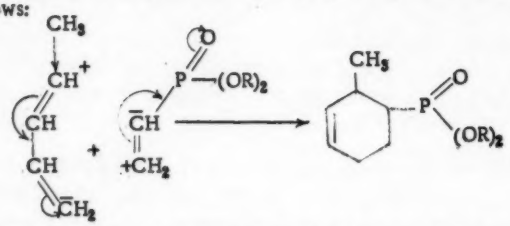
No.	Formula	B.p. (°C)	Pressure, mm Hg	n_D^{20}	d_4^{20}	Yield, %
1	$(C_2H_5O)_2P(O)-CH_2-CH_2-SH$	95-96	3	1,4210	1.0392	75.0
2	$(C_2H_5O)_2P(O)-CH_2-CH_2-SC_2H_5$	96	3	1.4265	1.0406	63.8
3	$(C_4H_9O)_2P(O)-CH_2CH_2SC_2H_5$	165-167	7	1.4580	1.0109	78.0

These addition products – diethyl 2-mercaptoethylphosphonate, diethyl 2-ethylmercaptoethylphosphonate, and dibutyl 2-ethylmercaptoethylphosphonate – are liquids having an unpleasant odor characteristic of aliphatic sulfides, but weaker; they are insoluble in water, but of good solubility in alcohol.

We then proceeded to the study of the diene-synthesis reaction, using vinylphosphonic esters as dienophilic components. This type of diene synthesis has not been studied before. It is of interest on this account and is also of great interest in the chemistry of organophosphorus compounds since it makes possible the synthesis of phosphonic esters containing a cyclohexenyl radical. In this work we used piperylene and hexadiene as dienes. The first exploratory experiments already showed that vinylphosphonic esters are considerably less reactive as dienophiles than, for example, α,β-unsaturated aldehydes, ketones, nitriles, and esters are. In order to obtain satisfactory yields in the reactions with piperylene and hexadiene, it was necessary to continue the reaction for 25-30 hours at temperatures of 170-180° and 270-280° respectively. With regard to the structures of the products obtained, no doubts arise in the case of the reaction with hexadiene, which, being symmetrical, may be expected to form only one adduct, the diethyl (dibutyl) ester of 2,5-dimethyl-3-cyclohexenylphosphonic acid:



but in the case of the reaction with piperylene two isomeric adducts are theoretically possible: esters of 2-methyl-3-cyclohexenylphosphonic and 5-methyl-3-cyclohexenylphosphonic acids. Recent investigations of B.A.Arbuzov and Kataev [5] and of A.A.Petrov and coworkers [6] have shown that the direction of addition of dienophiles to unsymmetrical dienes is in good agreement with the concepts of electronic theory. In our investigation, as in the investigations of these authors, the diene synthesis with piperylene yielded only one adduct, the formation of which may be represented as follows:



The constants and yields of substances obtained by the diene synthesis are given in Table 2.

The adducts obtained are liquids having a weak but unpleasant odor. They are of poor solubility in water, but dissolve readily in alcohol and ether.

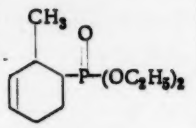
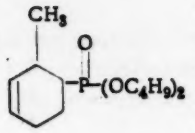
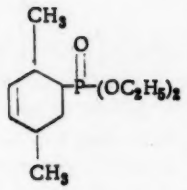
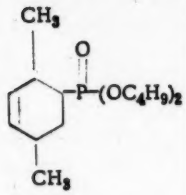
EXPERIMENTAL

Action of Tributyl Phosphite on Ethylene Dibromide

The reaction was carried out in a round-bottomed flask provided with dropping funnel and Widmer fractionating column, which was joined to a condenser for the condensation of butyl bromide. Tributyl phosphite (30 g) was

placed in the flask and was heated until the bath temperature reached 170°, when ethylene dibromide was slowly dropped in. During the reaction, the bath temperature was maintained at 170-190°. Altogether, 150 g of ethylene dibromide was added: a considerable amount of this was driven off during the reaction together with butyl bromide, for the boiling points of these two substances are very close together. Butyl bromide ceased to come over after 3 hrs. 30 min. Ethylene dibromide was driven off from the reaction mixture, and the residue was vacuum-distilled. After several fractionations we obtained about 2 g of dibutyl butylphosphonate and 19.8 g of dibutyl 2-bromoethylphosphonate, b.p. 146-147° at 5 mm; n_D^{20} 1.4485; d_4^{20} 1.1400. However, analysis for phosphorus and molecular-refraction calculations showed that the product obtained was not completely pure and contained, evidently, a small amount of dibutyl butylphosphonate (calculated %: P 10.3; found %: P 10.9), which boils at a temperature close to the boiling point of the main product.

TABLE 2

No.	Formula	B.p. °C	Pressure (mm Hg)	n_D^{20}	d_4^{20}	Yield %
1		118-119	3	1.4488	1.0166	63.5
2		155-156	3	1.4801	1.0379	65.2
3		125-127	7	1.4505	0.9992	44.0
4		156-157	2	1.4710	1.0042	36.4

From the residue we isolated 2.5 g of tetrabutyl 1,2-ethylenediphosphonate, b.p. 207-210°/7 mm; n_D^{20} 1.4402; d_4^{20} 1.0240; calculated MR_D 107.0; found MR_D 106.6.

Found %: P 15.3 $C_{18}H_{40}O_6P_2$. Calculated %: P 15.0.

An attempt was made to carry out the reaction by addition of the reactants in the reverse order, i.e., addition of tributyl phosphite to ethylene dibromide. However, the reaction did not go, for the temperature of the mixture did not attain the necessary value (170-190°).

Action of Alcoholic Potash on Dibutyl 2-Bromoethylphosphonate

An alcoholic solution of caustic potash (2.5 g) was added slowly (dropwise) to dibutyl 2-bromoethylphosphonate (15 g) dissolved in absolute ethanol (100 ml), the reaction mixture being stirred vigorously and cooled by surrounding the flask with ice. Addition of the alkali was accompanied by precipitation of potassium bromide. When reaction was complete, the precipitate was filtered off, and the alcohol was distilled from the filtrate. Vacuum distillation of the residue yielded dibutyl vinylphosphonate (7 g, 75%) having b.p. 115-116° at 5 mm; n_D^{20} 1.4372; d_4^{20} 0.9810; calculated MR_D 58.78; found MR_D 58.77.

Found %: P 14.4. $C_{10}H_{21}O_3P$. Calculated %: P 14.1

Action of Trimethyl Phosphite on Ethylene Dibromide

Trimethyl phosphite (40.5 g) and ethylene dibromide (100 g) were heated in a flask provided with a column for the removal of methyl bromide formed in the reaction. When the bath temperature reached 150°, profuse evolution of methyl bromide began; it was collected in a receiver cooled with a freezing mixture (10 g was collected). Fractionation of the reaction mixture yielded ethylene dibromide (50 g), trimethyl phosphite (15 g), and dimethyl methylphosphonate, b.p. 66-68°/8 mm; n_D^{20} 1.4135; d_4^{20} 1.1684.

The constants given in the literature [6] are: b.p. 181°/760 mm; n_D^{20} 1.4146; d_4^{20} 1.1684. There was a resinous residue, which decomposed when attempts were made to fractionate it under reduced pressure.

Addition of Hydrogen Sulfide to Diethyl Vinylphosphonate

Hydrogen sulfide was passed at room temperature through a solution of diethyl vinylphosphonate (6 g) in absolute ethanol (42 g) containing sodium ethoxide (0.3 g), until the mixture was completely saturated. After the mixture had stood for one day at room temperature, the alcohol was driven off, and the residue was vacuum-distilled, yielding 3 g of the originalvinylphosphonic ester and 2.5 g of diethyl 2-mercaptoethylphosphonate, which had b.p. 95-96°/3 mm; n_D^{20} 1.4210; d_4^{20} 1.0392; calculated MR_D 48.46; found MR_D 48.25.

Found %: P 15.30
$C_6H_{15}O_3SP$. Calculated %: P 15.62

In a second experiment the reaction was carried out in a sealed tube heated on a water bath for 15 hours. The yield was increased to 75%.

Addition of Ethanethiol to Diethyl Vinylphosphonate

A mixture of diethyl vinylphosphonate (5 g) and ethanethiol (4 g) was heated in presence of sodium ethoxide (0.3 g) in a sealed tube on a water bath for 18 hours. The tube was opened, the excess of ethanethiol was distilled off, and the residue was fractionated, yielding diethyl 2-ethylmercaptoethylphosphonate, b.p. 95-96°/4 mm; n_D^{20} 1.4265; d_4^{20} 1.0406; calculated MR_D 55.51; found MR_D 55.73.

Found %: P 13.72
$C_8H_{19}O_3PS$. Calculated %: P13.70

Addition of Ethanethiol to Dibutyl Vinylphosphonate

The reaction of dibutyl vinylphosphonate (5 g) with ethanethiol (4.5 g) in presence of sodium butoxide was carried out in a sealed tube heated in a water bath. Fractionation of the reaction mixture yielded dibutyl 2-ethylmercaptoethylphosphonate, b.p. 165-167°/7 mm; n_D^{20} 1.4580; d_4^{20} 1.0109; calculated MR_D 75.98; found MR_D 76.12.

Found %: P 11.4
$C_{12}H_{27}O_3PS$. Calculated %: P 11.0

Diene-synthesis Reactions of Piperylene and Hexadiene with Vinylphonic Esters

1. Reaction between piperylene and diethyl vinylphosphonate. A mixture of diethyl vinylphosphonate (7 g) and piperylene (10 g) was heated in presence of quinol (0.1 g) in a sealed tube at 170-180° for 25 hours. The excess of piperylene was distilled off, and the residue was vacuum-distilled, yielding some dimer of piperylene (about 3 g), unchanged vinylphosphonic ester (3.5 g), and diethyl 2-methyl-3-cyclohexenylphosphonate (3.5 g), which after two fractionations had b.p. 118-119°/3 mm; n_D^{20} 1.4488; d_4^{20} 1.0166; calculated MR_D 61.2; found MR_D 61.1. The residue was a resin.

Found %: P 13.40
$C_{11}H_{21}O_3P$. Calculated %: P 13.36

2. Reaction between piperylene and dibutyl vinylphosphonate. A mixture of dibutyl vinylphosphonate (3.7 g), piperylene (14 g), and quinol (0.1 g) was heated in a sealed tube at 190-200° for 25 hours. When the piperylene and its dimer had been driven off, the residue was distilled twice in a high vacuum and yielded dibutyl 2-methyl-3-cyclohexenylphosphonate, b.p. 155-156°/3 mm; n_D^{20} 1.4801; d_4^{20} 1.0379; calculated MR_D 79.7; found MR_D 78.8. The residue was a resin

Found %: P 11.0
$C_{15}H_{29}O_3P$. Calculated %: P 10.8

3. Reaction between hexadiene and diethyl vinylphosphonate. A mixture of diethyl vinylphosphonate (3 g), 2,4-hexadiene (10 g), and quinol (0.1 g) was heated in a sealed tube at 250-270° for 25 hours. Fractionation of the reaction mixture yielded diethyl 2,5-dimethyl-3-cyclohexenylphosphonate, b.p. 125-127°/7 mm; n_D^{20} 1.4505; d_4^{20} 0.9992; calculated MR_D 65.82; found MR_D 66.23.

Found %: P 12.7
$C_{12}H_{23}O_3P$. Calculated %: P 12.6

4. Reaction between hexadiene and dibutyl vinylphosphonate. A mixture of dibutyl vinylphosphonate (4 g) and hexadiene (10 g) was heated at 270-290° for 25 hours. Fractionation of the reaction mixture yielded some unchanged hexadiene, some dimer of hexadiene, some unchanged vinylphosphonic ester (about 0.5 g),

and dibutyl 2,5-dimethyl-3-cyclohexenylphosphonate (2 g) having b.p. 154-156°/3 mm; n_D^{20} 1.4710; d_4^{20} 1.0042; calculated MR_D 84.29; found MR_D 84.06.

Found %: P 10.5

$C_{16}H_{31}O_3P$. Calculated %: P 10.3

SUMMARY

1. Dibutyl vinylphosphonate has been synthesized.

2. It has been shown that vinylphosphonic esters combine at the double bond with hydrogen sulfide and with mercaptans, yielding the corresponding dialkyl 2-mercaptoethylphosphonates and dialkyl 2-alkylmercaptoethylphosphonates respectively.

3. It has been shown that vinylphosphonic esters may be used as dienophiles in diene-synthesis reactions. A method has been developed for the preparation of esters of homologs and derivatives of cyclohexenylphosphonic acid.

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LITERATURE CITED

[1] Hamilton, U. S. Patent 2365466 and 2382309; G. Kosolapoff, U. S. patent 2389576 (Chem. Abs. 40, 1536, 1946); Toy, U. S. patent 2425766; E. Bergman and A. Bondi, Ber. 64, 1455 (1931); 66. 286 (1933); A. Ford-Moore and Williams, J. Chem. Soc. 1947, 1465.

[2] M. I. Kabachnik, Bull. Acad. Sci. USSR, Div. Chem. Sci. 223 (1947).

[3] G. Kosolapoff, J. Am. Chem. Soc. 70, 1971 (1948).

[4] A. N. Pudovik, Proc. Acad. Sci. USSR, 80, 65 (1951).

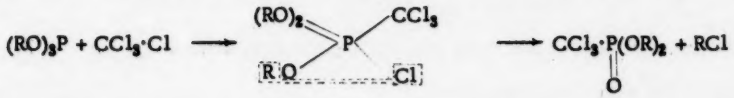
[5] B. A. Arbuzov and E. G. Kataev, J. Gen. Chem. 20, 68 (1950). See Consultants Bureau translation, p.73.

[6] A. A. Petrov and coworkers, J. Gen. Chem., 17, 538, 1295, 1543 (1947); 18, 424, 1781, 2228 (1948).

DECHLORINATION OF HEXACHLOROETHANE BY TRIALKYL PHOSPHITES

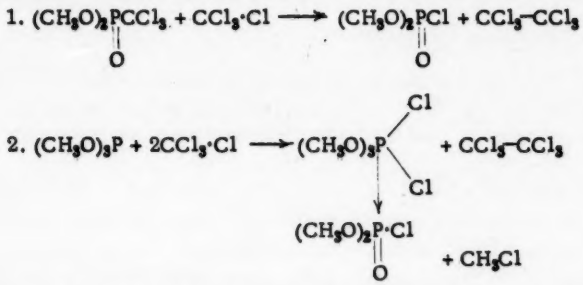
Gilm Kamai

In a number of previous papers [1] it has been shown that carbon tetrachloride reacts fairly readily with many alkyl esters of phosphorous, alkylphosphonous, dialkylphosphinous, arylphosphonous, diarylphosphinous, pyrophosphorous, and hypophosphoric acids. Trialkyl phosphites react mainly according to the following scheme:



However, the lowest member of these esters, trimethyl phosphite, forms an exception: it reacts with carbon tetrachloride in a more complicated fashion.

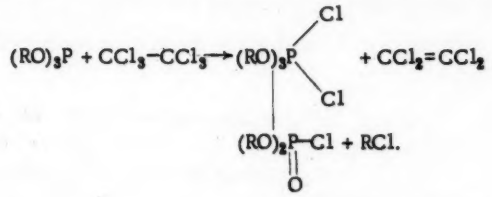
Reaction in accordance with the above scheme between trimethyl phosphite and carbon tetrachloride in equimolecular amounts will yield methyl chloride and methyl trichloromethylphosphonite, but it is probable that the latter ester then reacts with another molecule of carbon tetrachloride, forming hexachloroethane and dimethyl phosphorochloridate (Equation 1), or with two molecules of carbon tetrachloride, when intermolecular dechlorination occurs (Equation 2):



It is interesting to note that trimethyl phosphite is here acting similarly to aluminum amalgam as a dechlorination agent in the formation of hexachloroethane from carbon tetrachloride.

It was considered that, if this second, intermolecular-dechlorination reaction did in fact occur, then it would undoubtedly be of interest to study the reaction between phosphorous esters and hexachloroethane itself.

With this object, experiments were carried out on the reactions of hexachloroethane with trimethyl, tripropyl, triisopropyl, and tributyl phosphites. As a result of these experiments it was established that, on being heated with an alkyl phosphite, hexachloroethane reacts very vigorously with formation of the corresponding alkyl chloride and dialkyl phosphorochloridate and of tetrachloroethylene. The reaction scheme is probably as follows:



EXPERIMENTAL

Action of Hexachloroethane on Tributyl Phosphite

A mixture of tributyl phosphite (15 g) and hexachloroethane (14.2 g) was heated cautiously in the distilling flask of an Arbuzov assembly. At a bath temperature of about 100-105° the reaction became very vigorous with

evolution of a substance of b.p. 78.5°, and external cooling was applied. By slow heating of the reaction mixture, Fraction I (5.3 g) of b.p. 78-80° and d_0^0 0.9069 was isolated; according to its properties, this fraction was relatively pure butyl chloride. The liquid remaining in the flask was vacuum-distilled; first at 28-30 mm (water pump), when Fraction II (6.8 g) came over at 38-40°; then at 4 mm (oil pump, when Fractions III (4.3 g) (b.p. 81-102°) and IV (7 g) (b.p. 102-104°)came over.

Redistillation of Fraction II yielded a liquid boiling at 121° under normal pressure; it had n_D^{20} 1.4998 and d_0^0 1.6298. According to its constants the substance was tetrachloroethylene.

Further fractionation of fractions III and IV yielded a substance of b.p. 132-133°/15 mm; d_0^0 1.1442 and n_D^{20} 1.4341.

Found %: P 13.48

$C_8H_{18}ClO_3P$. Calculated %: P 13.76

According to the analytical data, this substance was dibutyl phosphorochloridate.

Action of Hexachloroethane on Tripropyl phosphite

A mixture of tripropyl phosphite (15 g) and hexachloroethane (17 g) was heated slowly on an oil bath. Reaction set in at a bath temperature of about 100° with separation of propyl chloride. Fractionation yielded a propyl chloride fraction (4.9 g) of b.p. 46-47° and d_0^0 0.911 and a tetrachloroethylene fraction (9.1 g) of b.p. 121°; from the higher fractions a substance (6.8 g) of b.p. 107-108°/13 mm was isolated.

Found %: P 15.39

$C_6H_{14}ClO_3P$. Calculated %: P 15.47

Thus, according to the analytical data for phosphorus, the substance was dipropyl phosphorochloridate.

Action of Hexachloroethane on Triisopropyl phosphite

Careful heating of a mixture of triisopropyl phosphite (15 g) with hexachloroethane (16.9 g) yielded an isopropyl chloride fraction, b.p. 35-36° and d_0^{20} 0.8677, and a tetrachloroethylene fraction (8.9 g), b.p. 121°. Attempts to isolate diisopropyl phosphorochloridate from the higher fractions were not successful.

Action of Hexachloroethane on Trimethyl Phosphite

A mixture of trimethyl phosphite (12.4 g) and hexachloroethane (23.7 g) was heated cautiously in a flask fitted with reflux condenser. When the bath temperature reached about 90°, a very vigorous reaction set in, and it was therefore necessary to discontinue heating temporarily and to apply external cooling. The mixture was finally heated again for about two hours. The flask and contents were weighed before and after the heating, and the loss in weight was 6.9 g, instead of the theoretically required 5 g of methyl chloride. Fractional distillation yielded a tetrachloroethylene fraction (about 10 g). An attempt to separate dimethyl phosphorochloridate in the pure state was not successful.

I acknowledge my great indebtedness to L. A. Koroleva for the help she has given me in the experimental part of this work.

SUMMARY

1. It has been shown that, when trialkyl phosphites react with hexachloroethane, the corresponding alkyl chlorides and dialkyl phosphorochloridates are formed together with tetrachloroethylene.

2. It has been established that trialkyl phosphites may be used as dechlorinating agents for highly chlorinated paraffins.

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LITERATURE CITED

[1] Gilm Kamai, Proc. Acad. Sci. USSR, 55, 228 (1947); J. Gen. Chem. 16, 1522 (1946); Proc. Acad. Sci. USSR, 66, 388 (1949); 70, 233 (1950); 79, 795 (1951).

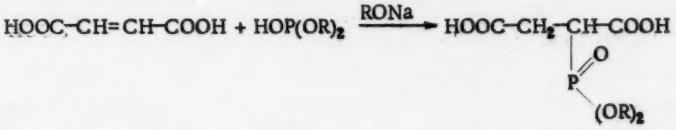
NEW METHOD FOR THE SYNTHESIS OF PHOSPHONIC AND PHOSPHINIC ESTERS AND THEIR THIO ANALOGS

COMMUNICATION 12. ADDITION OF DIALKYLPHOSPHOROUS ACIDS TO UNSATURATED DIBASIC ACIDS AND THEIR ESTERS

A. N. Pudovik

I have shown in previous papers [1] that dialkylphosphorous acids add very readily to esters of α,β-unsaturated monobasic acids in presence of alkali-metal alkoxides with formation of the corresponding β-dialkoxyphosphinyl carboxylic esters (esters of β-carboxyalkylphosphonic acids). Also, we have prepared, just as readily and in good yields, addition products formed by dialkylphosphorous acids with esters of ethylidenemalonic, benzylidene malonic, and acetoacetic esters.

We considered that it was of interest, as a development of our new method for the synthesis of phosphonic and phosphinic esters and, in particular, as a development of the investigations referred to above, to study the addition of dialkylphosphorous acids to certain symmetrical unsaturated dibasic acids and their esters. The unsaturated compounds that we chose for study were maleic and fumaric acids and their esters, and diethyl acetylenedicarboxylate. The reactions were carried out in presence of alkali-metal alkoxides in accordance with the usual procedure, which is described in detail in previous papers. Dialkylphosphorous acids in their reactions with maleic acid, to which they added very readily with considerable evolution of heat, showed behavior that contrasted sharply with that shown in previous, unsuccessful experiments on their addition to α,β-unsaturated monobasic acids. Dimethoxy- and diethoxy-phosphinylsuccinic acids were prepared in satisfactory yield.

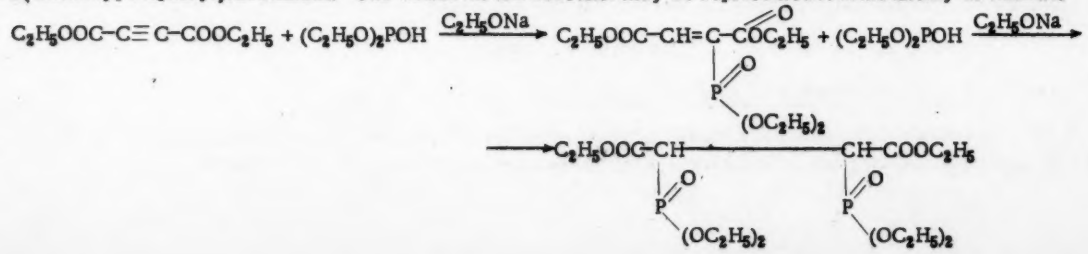


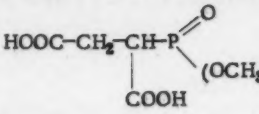
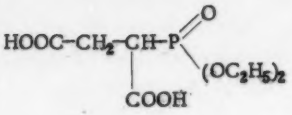
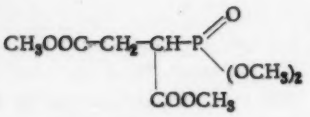
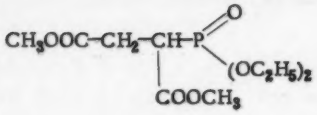
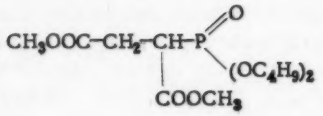
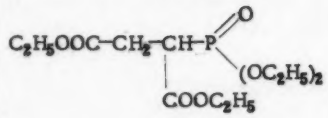
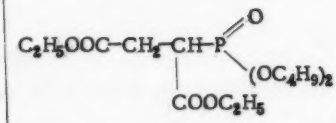
Dialkylphosphorous acids add to maleic anhydride just as vigorously, but decomposition occurs during the vacuum distillation of the reaction mixture, low-boiling products being formed.

Addition of dialkylphosphorous acids to maleic esters in presence of alkali-metal alkoxides proceeds very vigorously and is accompanied by a change in color of the reaction mixture and the evolution of much heat. Addition of dialkylphosphorous acids to fumaric ester proceeds just as vigorously. Constants and yields of the addition products formed by dialkylphosphorous acids with maleic acid, dimethyl maleate, and diethyl fumarate are given in the table.

Attempts to bring about the addition of dialkylphosphorous acids to diethyl chlorofumarate, under our usual experimental conditions and also in presence of piperidine, were not successful.

Finally, a study was made of the addition of dialkylphosphorous acids to diethyl acetylenedicarboxylate. It might be expected that, depending on the ratio of reactants and experimental conditions, one or two molecules of dialkylphosphorous acid would add at the triple bond of acetylene dicarboxylic ester. Actually, when the molar ratio of diethylphosphorous acid to acetylenedicarboxylic ester was 2:1, only one addition product was obtained, and analysis for phosphorus, which was in accord with the empirical formula $C_{16}H_{32}O_{10}P_2$, indicated it to be diethyl bis(diethoxyphosphinyl)succinnate. The course of the reaction may be represented schematically as follows:



No.	Formula	B.p. °C	Pressure (mm Hg)	n_D^{20}	d_4^{20}	Yield %
1		141	3	1.4428	1.2695	50.0
2		137-138	1	1.4408	1.1782	70.8
3		142	2	1.4435	1.2076	78.0
4		184	13	1.4422	1.1803	81.9
5		161-162	1	1.4425	1.0666	69.7
6		161-162	2	1.4410	1.1333	82.3
7		178-179	2	1.4417	1.0673	95.7

A consideration of steric factors operating during the reaction indicates that the two diethoxyphosphinyl groups are probably attached to different carbon atoms, although their positions in the addition product were not determined precisely.

In a second experiment, carried out with the object of preparing the addition product formed from one molecule of diethylphosphorous acid and one of acetylenedicarboxylic ester, the reaction was performed in alcoholic solution and the amount of diethylphosphorous acid taken was half of that used before. However, also in this experiment, the only pure product obtained was bis(diethoxyphosphinyl)succinic ester; attempts to isolate a pure product from the low-boiling fraction (125-185°/8 mm) were not successful, in spite of repeated refractionations, for, although a fraction (b.p. 160-163°/3 mm) was obtained in small quantity and evidently consisted mainly of the required substance, it was contaminated (the discrepancy between the calculated and found phosphorus contents was about 1%).

Similarly, in the reaction between diethyl acetylenedicarboxylate and dimethylphosphorous acid, only diethyl bis(dimethoxyphosphinyl)succinate was obtained in the pure state.

EXPERIMENTAL

Addition of Dimethylphosphorous Acid to Maleic Acid

A saturated solution of sodium methoxide in absolute methanol was added dropwise to a mixture of maleic acid (4.2 g) and dimethylphosphorous acid (8 g). Addition of each drop resulted in a considerable rise in the

temperature of the reaction mixture. Altogether, about ten drops were added, and further addition of methoxide did not produce a heating effect. Fractionation of the reaction mixture yielded dimethoxyphoshpinylsuccinic acid (4.1 g) having b.p. 141°/3 mm; n_D^{20} 1.4428; d_4^{20} 1.2695.

Found %: P 13.7; 13.9
$C_6H_{11}O_7P$. Calculated %: P 13.7

Addition of Diethylphosphorous Acid to Maleic Acid

Maleic acid (3 g) and diethylphosphorous acid (6 g) were taken for reaction, and ethanol was added to the mixture until the maleic acid was completely dissolved. The reaction was carried out in presence of sodium ethoxide. The reaction mixture was heated on a water bath for three hours; the alcohol was then distilled off, and the residue was vacuum-fractionated, yielding diethoxyphosphinylsuccinic acid (4.6 g) having b.p. 137°-138° at 1 mm; n_D^{20} 1.4408; d_4^{20} 1.1782.

Found %: P 12.1; 12.0
$C_8H_{15}O_7P$. Calculated %: P 12.2

Addition of Dialkylphosphorous Acids to Maleic Anhydride

A mixture of maleic anhydride (8 g) and dimethylphosphorous acid (12 g) was heated in an Arbuzov flask on a water bath until the maleic anhydride had melted and dissolved. A solution of sodium methoxide in methanol was then added dropwise: evolution of heat occurred, but was not as great as in the maleic acid reaction. In the fractionation the temperature of the vapor rose to 105-110° at 7 mm pressure, and then vigorous decomposition set in. An attempt to add diethylphosphorous acid to maleic anhydride was also unsuccessful.

Addition of Dimethylphosphorous Acid to Dimethyl Maleate

Dimethyl maleate (7.2 g) and dimethylphosphorous acid (6 g) were taken for reaction. Addition of the first few drops of a solution of sodium methoxide in methanol brought about an extremely vigorous reaction accompanied by evolution of much heat and boiling of the reaction mixture (vaporization of methanol). The temperature of the reaction mixture rose to 70°. Further addition of methoxide was carried out while the mixture was cooled with water. Sufficient (about 20 drops in all) of the saturated sodium methoxide solution was added to complete the reaction, and the mixture was then heated for one hour on a water bath. It was then vacuum-fractionated: two fractionations yielded dimethyl dimethoxyphosphinylsuccinate (9.9 g) having b.p. 142°/2 mm; n_D^{20} 1.4435; d_4^{20} 1.2076.

Found %: P 11.9
$C_8H_{15}O_7P$. Calculated %: P 12.2

Addition of Diethylphosphorous Acid to Dimethyl Maleate

Dimethyl maleate (14.7 g) and diethylphosphorous acid (14 g) were taken for reaction, the catalyst being a solution of sodium ethoxide in ethanol. The procedure was similar to that of the preceding experiment, and fractionation of the reaction mixture yielded dimethyl diethoxyphosphinylsuccinate (23.6 g) having b.p. 184°/13 mm; n_D^{20} 1.4422; d_4^{20} 1.1803.

Found %: P 10.9; 10.8
$C_{10}H_{19}O_7P$. Calculated %: P 10.9

Addition of Dibutylphosphorous Acid to Dimethyl Maleate

Dibutylphosphorous acid (15 g) reacted with dimethyl maleate (10.7 g) in presence of sodium butoxide. Fractionation of the reaction mixture yielded dimethyl dibutoxyphosphinylsuccinate (17.9 g) having b.p. 161-162° at 1 mm; n_D^{20} 1.4425; d_4^{20} 1.0666.

Found %: P 8.8; 8.9
$C_{14}H_{27}O_7P$. Calculated %: P 9.2

Hydrolysis of Dimethyl Diethoxyphosphinylsuccinate

The ester (3.5 g) was hydrolyzed with dilute (1:1) hydrochloric acid in a sealed tube at 120-130° for six hours. Ethyl chloride was removed from the solution, which was then heated on a water bath, distilled water

being added periodically to make up for losses by evaporation. When the whole of the hydrogen chloride present had been removed, the solution was carefully evaporated down, yielding dihydroxyphosphinylsuccinic acid as a thick yellowish oil, which did not crystallize after long standing in a desiccator (either at room temperature or under cooling).

Addition of Diethylphosphorous Acid to Diethyl Fumarate

Fumaric ester (6.8 g) and diethylphosphorous acid (6.5 g) were taken for reaction. Addition of ethoxide was accompanied by evolution of much heat. Fractionation yielded diethyl diethoxyphosphinylsuccinate (10.2 g) having b.p. 161-162°/2 mm, n_D^{20} 1.4410; d_4^{20} 1.1333.

Found %: P 10.3, 10.2

$C_{12}H_{23}O_7P$. Calculated %: P 10.0

Addition of Dibutylphosphorous Acid to Diethyl Fumarate

Fumaric ester (5.1 g) reacted with dibutylphosphorous acid (6 g) in presence of sodium butoxide, yielding diethyl dibutoxyphosphinylsuccinate (9.1 g) having b.p. 178-179° at 2 mm; n_D^{20} 1.4417; d_4^{20} 1.0673.

Found %: P 8.6

$C_{16}H_{31}O_7P$. Calculated %: P 8.5

Addition of Diethylphosphorous Acid to Diethyl Acetylenedicarboxylate

Expt. 1. Diethyl acetylenedicarboxylate (5.6 g) and diethylphosphorous acid (9.2 g) were taken for reaction. No heating effect occurred when the first few drops of ethoxide solution were added, but further addition caused the liquid to turn violet, and the mixture began to warm up rapidly, the temperature rising to 88°. The mixture was cooled and fractionated, yielding diethyl bis(diethoxyphosphinyl)succinate (6 g) having b.p. 213-214° at 5 mm; n_D^{20} 1.4700; d_4^{20} 1.3753.

Found %: P 14.1; 13.9

$C_{16}H_{32}O_{10}P_2$. Calculated %: P 13.9

Expt. 2. The reaction mixture, which consisted of acetylenedicarboxylic ester (7 g), diethylphosphorous acid (5.8 g), ethanol (20 ml), and ethoxide solution (1 ml), was heated on a water bath for three hours. Fractionation of the reaction mixture yielded diethyl bis(diethoxyphosphinyl)succinate (2.7 g), b.p. 210°, having constants identical with those obtained in the first experiment, and a fraction (5.6 g) of b.p. 125-185°/8 mm. In a second fractionation it again boiled over a wide temperature range, but the top cut, which had a stable boiling point of 160-163°/3 mm, contained 9.1% of phosphorus, compared with 10% required for the product formed by addition of one molecule of diethylphosphorous acid to acetylenedicarboxylic ester.

Addition of Dimethylphosphorous Acid to Diethyl Acetylenedicarboxylate

Acetylenedicarboxylic ester (14 g) reacted with dimethylphosphorous acid (9.5 g) in presence of sodium methoxide. The reaction was very vigorous: the temperature of the reaction mixture rose rapidly to 105°, and the color of the mixture gradually changed from pink to dark red. Fractionation of the reaction mixture yielded diethyl bis(dimethoxyphosphinyl)succinate (3.2 g) having b.p. 200-203°/3 mm; n_D^{20} 1.4635; d_4^{20} 1.2715, and also a fraction (15.6 g) of b.p. 70-200°/6 mm, which after repeated fractionation still boiled over a wide range of temperature.

Found %: P 15.5

$C_{12}H_{24}O_{10}P_2$. Calculated %: P 15.9

SUMMARY

1. It has been shown that, in presence of alkali-metal alkoxides, dialkylphosphorous acids readily add to maleic acid and to maleic and fumaric esters. The addition products have been obtained in good yield (dialkoxyphosphinylsuccinic acids and their esters).

2. It has been shown that under the same conditions, dialkylphosphorous acids add to diethyl acetylenedicarboxylate, and the products formed by addition of two molecules of dialkylphosphorous acid [bis(dialkoxyphosphinyl)succinic esters] have been isolated.

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A. E. Arbuzov Chemical Institute of the Kazan Affiliated Institute of the USSR Academy of Sciences

LITERATURE CITED

[1] A. N. Pudovik, J. Gen. Chem. 21, 1837 (1951); 22, 467 (1952). *

* See Consultants Bureau translation, p. 2035; p. 531.

NEW METHOD FOR THE SYNTHESIS OF PHOSPHONIC AND PHOSPHINIC ESTERS AND THEIR THIO ANALOGS

COMMUNICATION 13. ADDITION OF O,O-DIETHYL HYDROGEN PHOSPHOROTHIOITE TO KETONES AND ALDEHYDES

A. N. Pudovik and G. A. Zametaeva

In a number of previous papers [1] one of us has shown that dialkylphosphorous acids add very readily to unsaturated aldehydes and ketones in presence of alkali-metal alkoxides. Unsaturated aldehydes combine with dialkylphosphorous acids at the carbonyl group with formation of α-hydroxy phosphonic esters, but unsaturated ketones react at the double bond with formation of keto phosphonic esters. Only when selective addition of the first molecule is complete does further addition begin at the double bond or carbonyl group respectively of a second molecule of dialkylphosphorous acid (if excess of this is present in the reaction mixture) with formation of a hydroxy diphosphonic acid.

In connection with these investigations we considered that it was of interest to study the addition of O,O-dialkyl hydrogen phosphorothioites to unsaturated aldehydes and ketones and to compare the behavior of these esters in addition reactions with that of the corresponding dialkyl hydrogen phosphites (dialkylphosphorous acids). Also, this study could lead to the development of a method for the preparation of compounds of a new type — various derivatives of phosphonothionic esters.

In the first series of experiments a study was made of the addition of O,O-diethyl hydrogen phosphorothioite to a number of unsaturated ketones; ethylideneacetone (3-penten-2-one), benzylideneacetone (4-phenyl-3-buten-2-one), furfurylideneacetone (4-furyl-3-buten-2-one), and mesityl oxide (4-methyl-3-penten-2-one). The reaction was carried out in presence of sodium ethoxide by the procedure described in previous papers. Addition proceeded very readily and was accompanied by a considerable evolution of heat. As in the addition of diethyl hydrogen phosphite to these compounds, it was found that reaction set in only after a definite amount of sodium ethoxide solution had been added and then went very rapidly, generally to completion. These peculiarities indicate that these reactions have certain definite characteristics: as we have pointed out previously, they proceed by a chain mechanism.

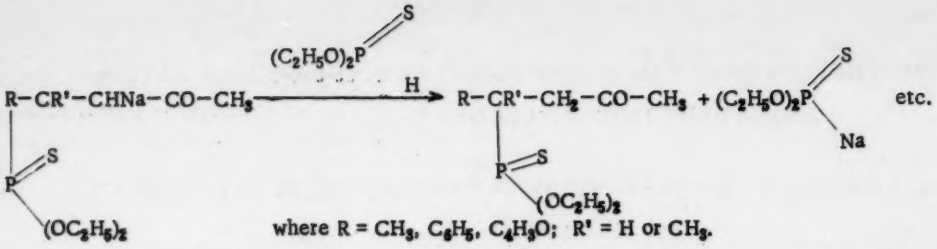
As in the reactions of dialkyl hydrogen phosphites, addition of O,O-diethyl hydrogen phosphorothioite proceeded most vigorously with ethylidene- and benzylidene-acetone, the addition products being obtained in 50-75% yield. An investigation of the properties of the addition products showed that they contained a free ketone group, for they formed phenylhydrazones and semicarbazones with phenylhydrazine and semicarbazide respectively; also, they were saturated: this was established by the aid of the bromination reaction. On the basis of these results the conclusion was reached that the products obtained were keto phosphonothionic esters and that addition of O,O-dialkyl hydrogen phosphorothioite to α,β-unsaturated ketones occurs in the first place at the double bond, which in these compounds is more active than the ketone group. The course of the addition reaction may be represented as follows:

$$(C_2H_5O)_2PSH + C_2H_5ONa \rightleftharpoons (C_2H_5O)_2P(=S)SNa + C_2H_5OH$$

$$R-\overset{+}{C}R'=CH-\overset{O^-}{C}-CH_3 + (C_2H_5O)_2\overline{P}(=S)SNa \longrightarrow R-CR'-CH=C(ONa)CH_3$$

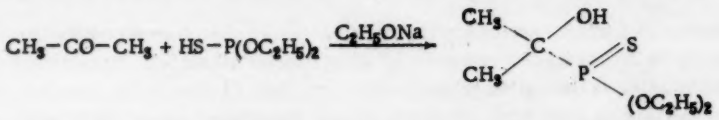
$$\text{with } CR'(P(=S)(OC_2H_5)_2) \text{ and } R = \text{furyl}$$

or



where R = CH_3, C_6H_5, C_4H_3O; R' = H or CH_3.

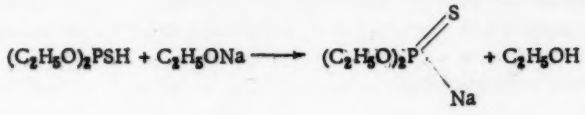
However, in the products obtained the ketone group also is able to combine with O,O-diethyl hydrogen phosphorothioite when there is an excess of the latter in the reaction mixture. We showed that this reaction is possible by special experiments on the simplest saturated ketone, acetone. Reaction went according to the equation

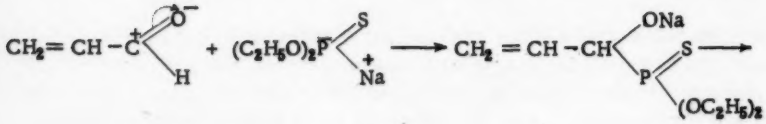


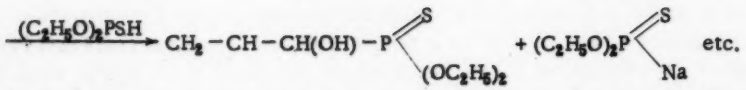
with formation of diethyl 1-hydroxy-1-methylethylphosphonothionate, i.e., in similar manner to the addition of dialkyl hydrogen phosphites to keto phosphonic esters, as noted in previous papers, and to the simplest saturated aldehydes and ketones, as described by Abramov [2]. Constants and yields of our addition products are given in Table 1.

A study was also made of the addition of O,O-diethyl hydrogen phosphorothioite to unsaturated and saturated aldehydes. Reactions with acrolein, crotonaldehyde, and 2-furanacrolein yielded addition products in about 50% yield, and it was found that they did not react with substances that readily react with the carbonyl group, including phenylhydrazine and semicarbazide.

Reaction with bromine indicated the presence of one double bond. The results obtained show definitely that the addition products formed by O,O-diethyl hydrogen phosphorothioite with unsaturated aldehydes are unsaturated α-hydroxy phosphonothionic esters and that addition therefore proceeds not at the double bond, as in unsaturated ketones, but at the carbonyl group. The course of the reaction may be represented as follows:







Similar experiments with acetaldehyde and butyraldehyde showed that addition of O,O-diethyl hydrogen phosphorothioite proceeds very readily also at the carbonyl group of a saturated aldehyde. Constants and yields of the addition products obtained—unsaturated and saturated α-hydroxy phosphonothionic esters—are given in Table 2.

From the investigations that we have carried out the conclusion may be drawn that in its addition reactions with unsaturated and saturated aldehydes and ketones O,O-diethyl hydrogen phosphorothioite exhibits the same specific reactivity as dialkyl hydrogen phosphites.

TABLE 1

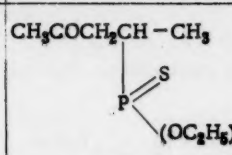
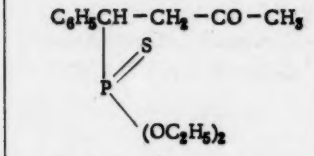
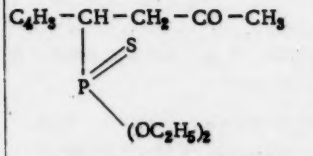
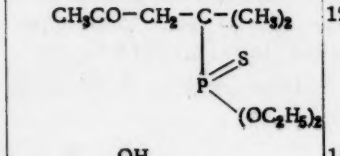
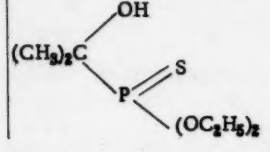
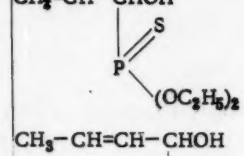
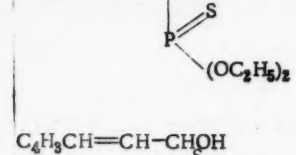
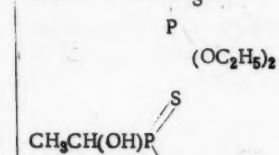
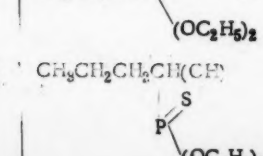
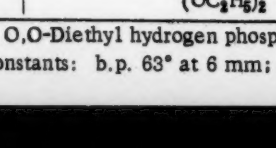
No.	Formula	B.p. (°C)	Pressure (mm Hg)	n_D^{20}	d_4^{20}	Yield (%)
1		142-144	12	1.4638	1.0549	50.1
2		177-178	7	1.5344	1.1462	46.5
3		164-166	7	1.5025	1.1471	48.7
4		128-130	7	1.4731	1.0590	74.1
5		107-109	10	1.4684	1.0735	62.1

TABLE 2

No	Formula	B.p. (°C)	Pressure (mm Hg)	n_D^{20}	d_4^{20}	Yield (%)
1		120-122	10	1.4828	1.1158	46.2
2		130-132	8	1.4846	1.1019	43.7
3		101-102	10	1.5280	1.0785	46.1
4		111-113	12	1.4721	1.1029	62.3
5		122-123	7	1.4781	1.0525	45.4

EXPERIMENTAL*

Addition of O,O-Diethyl Hydrogen Phosphorothioite to Ethylideneacetone. O,O-Diethyl hydrogen phosphorothioite (8 g) was caused to react with 4.4 g ethylideneacetone in presence of a saturated solution of sodium ethoxide. The reaction was accompanied by evolution of much heat. Thirty minutes after the completion of the reaction, the mixture was vacuum-distilled, yielding diethyl 1-methyl-3-oxobutylphosphonothionate (6.2 g) having b.p. 142-144/12 mm; n_D^{20} 1.4638; d_4^{20} 1.0549; found MR_D 62.23; calculated MR_D 62.22.

Found %: P 13.10
$C_9H_{19}O_3PS$. Calculated %: P 13.02

The addition product is a viscous, greenish oil of unpleasant odor.

Preparation of the phenylhydrazone. A mixture of the addition product (5 g), 2.3 g phenylhydrazine, and 6 ml absolute ethanol was placed in a porcelain dish and left in a desiccator for five days at room temperature. Vacuum distillation yielded 1.5 g of the phenylhydrazone of diethyl 1-methyl-3-oxobutylphosphonothionate (b.p. 238-240°/9 mm) as a thick, greasy, cherry-colored liquid. Some decomposition occurred during fractionation, and a dark-red resin remained as residue.

Found %: P 9.18, 8.99
$C_{15}H_{25}N_2O_2PS$. Calculated %: P 9.17

Preparation of the semicarbazone. Ethanol (5 ml) was added to a mixture of the addition product (1.5 g), semicarbazide hydrochloride (0.8 g) as an aqueous solution, and sodium acetate (0.6 g). The mixture was heated to boiling on a water bath, and was then

* O,O-Diethyl hydrogen phosphorothioite was prepared by the method developed in our laboratory; it had the following constants: b.p. 63° at 6 mm; n_D^{20} 1.4587; d_4^{20} 1.0763.

gradually cooled. After 2-3 hours white crystals (m.p. 124°) began to appear. Recrystallization from alcohol did not affect the melting point of the crystals obtained.

Found %: P 10.30

$C_{19}H_{22}N_3O_3PS$. Calculated %: P 10.51

Double-bond determination. A determination carried out by the McIlhiney method indicated an absence of double bonds.

Addition of O,O-Diethyl Hydrogen Phosphorothioite to Benzylideneacetone. The reaction was carried out with 5.3 g of O,O-diethyl hydrogen phosphorothioite and 5 g of benzylideneacetone in presence of sodium ethoxide, of which 15-20 drops were added in all; much heat was evolved. Fractionation of the reaction mixture yielded diethyl 1-phenyl-3-oxobutylphosphonothionate (4.6 g) having b.p. 177-178°/7 mm; n_D^{20} 1.5344; d_4^{20} 1.1462; found MR_D 81.41; calculated MR_D 81.7.

Found %: P 10.43

$C_{14}H_{21}O_3PS$. Calculated %: P 10.33

The addition product is a yellowish oil of unpleasant odor and of good solubility in alcohol and ether. A double-bond determination by the McIlhiney method showed that the substance is saturated.

Addition of O,O-Diethyl Hydrogen Phosphorothioite to Furfurylideneacetone. O,O-diethyl hydrogen phosphorothioite (6 g) reacted with furyfurylideneacetone (5 g) in presence of 10-15 drops of a saturated solution of sodium ethylate. Heat was evolved, but the mixture did not become heated to the same extent as in the ethylideneacetone and benzylideneacetone reactions. Fractionation yielded diethyl 1-furyl-3-oxobutylphosphonothionate (5.1 g) having b.p. 164-166°/7 mm; n_D^{20} 1.5025; d_4^{20} 1.1471; found MR_D 74.67; calculated MR_D 74.58.

Found %: P 10.78

$C_{12}H_{19}O_4PS$. Calculated %: P 10.69

The addition product is a pale-yellow, viscous liquid of unpleasant odor and of good solubility in alcohol and ether.

Addition of O,O-Diethyl Hydrogen Phosphorothioite to Mesityl Oxide. Sodium ethoxide (20 drops) was added to a mixture of O,O-diethyl hydrogen phosphorothioite (6.85 g) and mesityl oxide (5 g). Reaction set in, and the mixture became very hot. The mixture was heated on a water bath for 30 minutes and was then vacuum-fractionated, yielding diethyl 1,1-dimethyl-3-oxobutylphosphonothionate (8 g) having b.p. 128-130°/7 mm; n_D^{20} 1.4731; d_4^{20} 1.0590; found MR_D 66.76; calculated MR_D 66.84.

Found %: P 12.43

$C_{10}H_{21}O_3PS$. Calculated %: P 12.30

The addition product is a colorless mobile liquid of good solubility in alcohol and ether.

Preparation of the phenylhydrazone. A mixture of diethyl 1,1-dimethyl-3-oxobutylphosphonothionate (5.6 g), phenylhydrazine (2.4 g) and absolute ethanol (8 ml) was allowed to stand for ten days at room temperature and was then vacuum-fractionated, yielding the phenylhydrazone (5 g, 65.7%; b.p. 234-235°/12 mm), a light-brown, thick greasy liquid.

Found %: P 8.83; 8.84

$C_{16}H_{27}O_2N_2PS$. Calculated %: P 9.06

Preparation of the semicarbazone. The small amount of alcohol necessary to produce a clear solution was added to a mixture of diethyl 1,1-dimethyl-3-oxobutylphosphonothionate (2 g), semicarbazide hydrochloride (1.3 g) as an aqueous solution, and sodium acetate (1 g). The mixture was heated to boiling on a water bath and was then gradually cooled, first to room temperature, and then to 0°. After one hour, crystallization set in. The melting point of the crystals obtained was 121°, raised to 123° by recrystallization from alcohol.

Found %: P 10.39

$C_{11}H_{21}N_3O_3PS$. Calculated %: P 10.03

Addition of O,O-Diethyl Hydrogen Phosphorothioite to Acetone. Sodium ethoxide (25-30 drops) was added to a mixture of freshly distilled acetone (17 g) and O,O-diethyl hydrogen phosphorothioite (4.8 g).

Reaction did not begin until 15-18 drops of sodium ethoxide had been added, and when further additions were made it proceeded with slight warming of the mixture. The reaction mixture was heated on a water bath for two hours and was then vacuum-fractionated, yielding diethyl 1-hydroxy-1-methylethylphosphonothionate (4 g) having b.p. 107-109°/10 mm; n_D^{20} 1.4684; d_4^{20} 1.0735; found MR_D 54.93; calculated MR_D 54.50.

Found %: P 14.72

$C_7H_{17}O_3PS$. Calculated %: P 14.62

The addition product is a colorless liquid of unpleasant odor and of good solubility in alcohol and ether.

Found %: OH 7.9 (Tserevitinov's method)

Calculated %: OH 8.01

Addition of O,O-Diethyl Hydrogen Phosphorothioite to Acrolein. Sodium ethoxide (20 drops) was added slowly to a mixture of O,O-diethyl hydrogen phosphorothioite (10 g) and acrolein (quinol-stabilized, 3.6 g), contained in a water-cooled flask. Reaction set in, and the reaction mixture became very hot. The sodium ethoxide was neutralized with glacial acetic acid, and the mixture was then vacuum fractionated, yielding diethyl 1-hydroxy-2-propenylphosphonothionate (6 g) having b.p. 120-122°/10 mm; n_D^{20} 1.4828; d_4^{20} 1.1158; found MR_D 53.73; calculated MR_D 54.03.

Found %: P 15.03

$C_7H_{15}O_3PS$. Calculated %: P 14.76

The addition product is a greenish viscous liquid of unpleasant odor and of good solubility in alcohol and ether.

Action of phenylhydrazine. A mixture of the addition product (2.3 g), phenylhydrazine (1.2 g), and absolute ethanol (6 ml) was allowed to stand for six days at room temperature and was then vacuum-fractionated. Unchanged phenylhydrazine (1.1 g) was isolated.

Action of semicarbazide. A mixture of the addition product (0.5 g), semicarbazide hydrochloride (0.4 g), and sodium acetate (0.3 g) was heated to boiling on a water bath and was then gradually cooled. No semicarbazone was obtained.

Double-bond determination. Substance taken: 0.2654 g; thiosulfate required for titration of the bromine that underwent addition: 20 ml (T = 0.02318). The addition reaction should have required 0.2022 g of bromine; 0.2377 g was, in fact, required.

Addition of O,O-Diethyl Hydrogen Phosphorothioite to Crotonaldehyde. Saturated sodium ethoxide solution was added to a mixture of O,O-diethyl hydrogen phosphorothioite (4.4 g) and crotonaldehyde (2 g); the reaction mixture grew very hot. Fractionation of the reaction mixture yielded diethyl-1-hydroxy-2-butenylphosphonothionate (2.4 g) having b.p. 130-132°/8 mm; n_D^{20} 1.4846; d_4^{20} 1.1019; found MR_D 58.22; calculated MR_D 58.64.

Found %: P 13.46; 13.55

$C_8H_{17}O_3PS$. Calculated %: P 13.83

The addition product is a yellow, mobile liquid, soluble in alcohol and ether.

Double-bond determination. According to calculation, the addition reaction required 0.2408 g of bromide, and actually 0.2128 g of bromine was consumed.

Addition of O,O-Diethyl Hydrogen Phosphorothioite to 2-Furanacrolein. Sodium ethoxide was added to a mixture of O,O-diethyl hydrogen phosphorothioite (4 g) and 2-furanacrolein (3.2 g) dissolved in absolute alcohol (6 ml). The heating up of the reaction mixture was not so marked as in the case of acrolein. Fractionation of the reaction mixture yielded diethyl 3-furyl-1-hydroxy-2-propenylphosphonothionate (2.8 g) having b.p. 101-102°/10 mm; n_D^{24} 1.5280; d_D^{40} 1.0785.

Found %: P 11.51

$C_{11}H_{17}O_4PS$. Calculated %: P 11.23

The addition product is a thick, yellow liquid, which crystallizes on standing. The crystals melt at 25-26°.

Addition of O,O-Diethyl Hydrogen Phosphorothioite to Acetaldehyde. A saturated solution of sodium ethoxide (20 drops) was added to a mixture of O,O-diethyl hydrogen phosphorothioite (5 g) and freshly distilled acetaldehyde (1.5 g). The reaction mixture became very hot, but the effect was not so marked as in the case of the unsaturated aldehydes. The reaction mixture was set aside for one day and then vacuum-

fractionated, yielding diethyl 1-hydroxyethylphosphonothionate (4 g) having b.p. 111-113°/12 mm; n_D^{20} 1.4721; d_4^{20} 1.1029; found MR_D 50.28; calculated MR_D 49.88.

Found %: P 15.91

$C_6H_{15}O_3PS$. Calculated %: P 15.65

The addition product is a pale-yellow oil of unpleasant odor.

Addition of O,O-Diethyl Hydrogen Phosphorothioite to Butyraldehyde. O,O-Diethyl hydrogen phosphorothioite (6 g) and butyraldehyde (3 g) reacted in presence of sodium ethoxide; the reaction mixture became hot and more viscous. Fractionation yielded diethyl 1-hydroxybutylphosphonothionate (3.6 g) having b.p. 122-123°/7 mm; n_D^{20} 1.4781; d_4^{20} 1.0925; found MR_D 58.56; calculated MR_D 59.12.

Found %: P 13.59; 13.52

$C_8H_{19}O_3PS$. Calculated %: P 13.71

SUMMARY

1. It has been shown that O,O-diethyl hydrogen phosphorothioite in presence of sodium ethoxide reacts readily at the double bond of unsaturated ketones with formation of keto phosphonothionic esters. It adds to saturated ketones at the carbonyl group with formation of α-hydroxy phosphonothionic esters.

2. O,O-Diethyl hydrogen phosphorothioite adds at the carbonyl group of unsaturated and saturated aldehydes with formation, respectively, of unsaturated and saturated α-hydroxy phosphonothionic esters.

3. A method has been developed for the synthesis of keto phosphonothionic esters and of unsaturated and saturated α-hydroxy phosphonothionic esters.

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V. I. Ulyanov-Lenin Kazan State University

LITERATURE CITED

[1] A. N. Pudovik, Proc. Acad. Sci. USSR, 73,3,499 (1950); A. N. Pudovik and Yu. P. Kitaev, J. Gen. Chem. 22, 467 (1952); A. N. Pudovik and B. A. Arbuzov Proc. Acad. Sci. USSR 73, 327 (1950).

[2] V. S. Abramov, Proc. Acad. Sci. USSR, 73, 487 (1950).

* See Consultants Bureau translation, p. 531.

NEW METHOD FOR THE SYNTHESIS OF PHOSPHONIC AND PHOSPHINIC ESTERS AND THEIR THIO ANALOGS

COMMUNICATION 14. NEW METHOD FOR THE SYNTHESIS OF AMINO PHOSPHONIC ESTERS

A. N. Pudovik and M. V. Korchemkina

In this paper a new method is proposed for the synthesis of amino phosphonic esters; it consists in the addition of dialkylphosphorous acids to anils. Anils are very reactive compounds and will combine at the double bond with various substances. Thus the simplest anil, N-benzylideneaniline, combines with bromine (giving a dibromide), and also with sodium bisulfite, ketones, amines, acetoacetic and malonic esters, hydrogen cyanide, nitromethane, organomagnesium compounds, and a number of other substances [1]. The direction of addition is determined by the polarization of the benzylideneaniline molecule and may be represented by the following general equation:

$$RH + C_6H_5CH{=}N{-}C_6H_5 \rightarrow C_6H_5{-}\underset{\displaystyle R}{\underset{|}{CH}}{-}NH{-}C_6H_5,$$

where $R = -SO_3Na$, $-CH_2COR'$, $-CN$, $CH_3COCHCOOC_2H_5$, $-CH_2NO_2$

and R' is alkyl or aryl. In all cases the corresponding secondary aromatic amine derivatives are obtained.

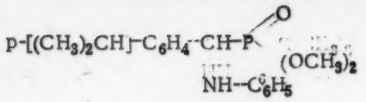
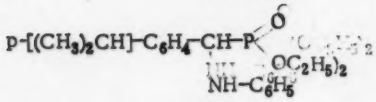
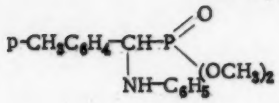
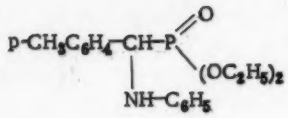
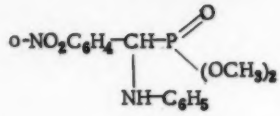
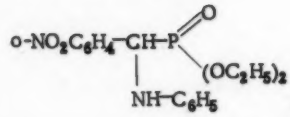
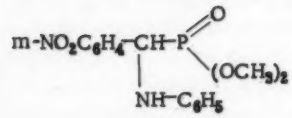
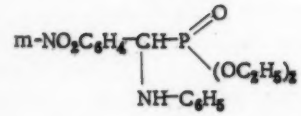
In connection with the investigations [2] carried out by one of us in the last few years on the addition of dialkylphosphorous acids to various unsaturated electrophilic reagents, for example, unsaturated ketones, aldehydes, nitriles, esters, acids, and vinylphosphonic esters, we considered that it was of great interest and importance to study the addition of dialkylphosphorous acids not only at double carbon — carbon and carbon — oxygen bonds, but also at double carbon — nitrogen bonds that are present in compounds of various types. We have embarked on this study, and have considered first the group of substituted aromatic imines obtained by the condensation of aromatic aldehydes and ketones with aniline derivatives. Preliminary work by Pudovik [3] has shown that, when the procedure that he has developed (reaction in presence of alkali-metal alkoxides [4]) is used, addition of dialkylphosphorous acids to the simplest anils (benzylideneaniline and certain of its derivatives) proceeds very readily, giving amino phosphonic esters in high yield. In our first series of experiments we have studied the addition of dimethyl- and diethyl-phosphorous acids to benzylideneaniline derivatives containing various substituents in the benzene nucleus of the benzylidene radical: (p-isopropyl-, (p-methyl-, (o-nitro-, (m-nitro-, and (o-hydroxy-benzylidene)aniline. The reaction was carried out in absolute ethanol in presence of sodium methoxide or ethoxide; the reaction mixtures became only slightly warm. The addition products were isolated by crystallization. Their melting points and yields, and the phosphorus-analysis results, are given in Table 1.

The addition products formed by dimethyl- and diethyl-phosphorous acids with (p-isopropylbenzylidene) aniline and (p-methylbenzylidene)aniline are white crystals of good solubility in ether and hot alcohol; they are insoluble in water. The addition products formed with (o- and (m-nitrobenzylidene)anilines are yellow substances. In the reactions of (o-hydroxybenzylidene)aniline (both with dimethyl- and with diethyl-phosphorous acid) a thick syrup was obtained which did not crystallize after long standing, and which decomposed when attempts were made to distil it under reduced pressure.

Further addition reactions of diethylphosphorous acid were carried out, namely, with N-benzylidine-p-chloroaniline and a number of anils having substituents in both benzene nuclei: N-(o-nitrobenzylidene)-m-toluidine, p-chloro-N-(p-isopropylbenzylidene)aniline, N-(p-methylbenzylidene)-m-toluidine, and N-(p-isopropylbenzylidene)-o-toluidine. The results obtained are given in Table 2.

All the reactions proceeded with slight evolution of heat. We synthesized the following anils derived from ketones in order to apply them in the addition reaction with diethylphosphorous acid: the anils derived from aniline

TABLE 1

No.	Formula	M.p. (°C)	Yield (%)	Phosphorus (%) found	Phosphorus (%) calculated
1		106-107	67.7	9.67	9.67
2		150	76.6	8.4; 8.70	8.59
3		121-122	77.8	10.40; 10.41	10.16
4		66	82.3	9.51; 9.62	9.31
5		175.5-176	77.2	9.57	9.22
6		155	87.7	8.41	8.51
7		130-131	82.8	9.67	9.22
8		93-94	90.9	8.64	8.51

and acetophenone, propiophenone, and benzophenone, acetophenone-m-toluidine anil, and acetophenone-o-toluidine anil. The reactions were carried out in presence of sodium ethoxide and with application of heat, for they went either slowly or not at all in the cold. However, only the addition products with acetophenone anil and propiophenone anil were obtained in crystalline form: in the remaining cases the products were thick syrups that did not crystallize on standing. The melting points and yields of the products obtained are given in Table 3.

We carried out also experiments on the addition of diethylphosphorous acid to benzylidenephenylhydrazine and certain of its derivatives, but in spite of long heating of the reaction mixture at 200°, the reaction did not go: only starting materials were isolated.

Finally, in view of the great variation in the ability of different anils to combine with diethylphosphorous acid, we decided to make a kinetic study of these reactions; in particular, we considered that it was of great interest to determine the effects of substituents in the benzene nuclei of the anils on the rate of dialkylphosphorous acid addition. We chose, as our first subject for investigation, the reaction between benzylideneaniline and diethylphosphorous acid. Concentrations of 0.725 –1.45 mole/liter were employed, and a 17.4% solution of sodium methoxide in absolute methanol was used as catalyst; the reaction was carried out in a thermostat at temperatures

TABLE 2

No.	Formula	B.p. °C	Yield %	Phosphorus (%) found	Phosphorus (%) calculated
1	$C_6H_5-CH(P(=O)(OC_2H_5)_2)-NH-C_6H_4Cl$-(p)	111-113	75.4	8.89	8.78
2	(m)-$NO_2-C_6H_4-CH(P(=O)(OC_2H_5)_2)-NH-C_6H_4CH_3$-(m)	129-130	78.7	8.51	8.20
3	(p)-$[(CH_3)_2CH]-C_6H_4-CH(P(=O)(OC_2H_5)_2)-NH-C_6H_4Cl$-(p)	119-119.5	82.7	7.93; 7.65	7.77
4	(p)-$CH_3-C_6H_4-CH(P(=O)(OC_2H_5)_2)-NH-C_6H_4-CH_3$-(m)	102-103	88.0	8.90	8.90
5	(p)-$[(CH_3)_2-CH]-C_6H_4-CH(P(=O)(OC_2H_5)_2)-C_6H_4-CH_3$-(o)	115	79.1	8.66	8.94

varying from that of the room to 70°. The course of the reaction was followed by titrating unchanged diethylphosphorous acid with 0.5 N caustic soda in presence of phenolphthalein. The first series of experiments, in which the alcohol used as solvent was rendered absolute by treatment with lime and sodium, did not give positive results: at low concentrations of catalyst the reactions did not go, and at high concentrations they went with evolution of much heat and were practically complete in a few seconds. It is evident that traces of water, present in the alcohol, had an effect on the reaction: decomposition occurred of the sodium diethylphosphite formed:

$$CH_3ONa + (C_2H_5O)_2POH \rightleftharpoons (C_2H_5O)_2P(=O)Na + CH_3OH$$

$$(C_2H_5O)_2P(=O)Na \xrightarrow{H_2O} (C_2H_5O)_2POH + NaOH$$

In succeeding experiments we therefore used alcohol that had been rendered absolute over sodium and then magnesium. Fig. 1 presents the results of experiments carried out with a 1.45 M solution of the reactants at 50° (total volume of reaction mixture, 50 ml). Curve I was obtained by the use of 0.5 ml of sodium methoxide solution, Curve II by the use of 1.0 ml, and Curve III, which coincides with the ordinate axis, by the use of 3.0 ml.

Similar results were obtained also when 0.725 M solutions were used at 30.4° (Fig. 2): Curve I, 2 ml; Curve II, 2.5 ml; and Curve III, 3 ml of sodium methoxide solution. As before, Curve III is practically coincident with the ordinate axis.

From these experiments theconclusion may be drawn that the addition reactions of dialkylphosphorous acids to benzylideneaniline are very sensitive to moisture. We have noted this on several occasions in the addition of dialkylphosphorous acids to other unsaturated compounds. At catalyst concentrations that ensure the formation in the reaction mixture of a sufficient amount of sodium diethylphosphite, the reaction goes extremely rapidly, being practically complete in a few seconds, and is accompanied by the generation of much heat. The specific course of these reactions can, in our opinion, be explained only by the assumption that they proceed by a chain mechanism, according to the scheme:

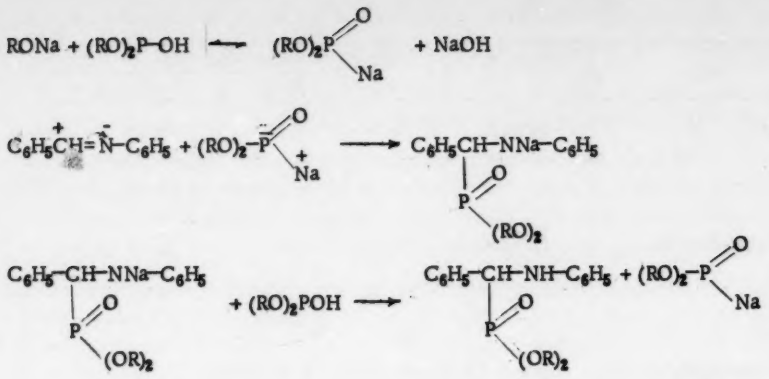
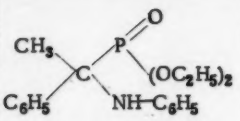
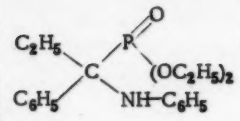


TABLE 3

No.	Formula	B.p. °C	Yield %	Phosphorus (%) found	Phosphorus (%) calculated
1		106-108	75	9.40	9.30
2		119-120	78.8	9.13	8.91

EXPERIMENTAL

General Procedure in Addition Reactions of Dialkylphosphorous Acids with Benzylideneaniline Derivatives

A saturated solution of sodium alkoxide in alcohol (15-20 drops) was added to a mixture of the benzylideneaniline derivative (3-4 g), an equimolecular amount of the dialkylphosphorous acid, and some absolute alcohol (a few milliliters, required to dissolve the anil). In order to avoid radical exchange, in the course of the reaction, between the dialkylphosphorous acid and the alkoxide, these reagents were chosen so as to have identical radicals. The reactions were generally accompanied by appreciable generation of heat. When the catalyst had been added, the reaction mixture was heated on a water bath for one hour and was then poured out into a porcelain dish. Depending on the nature of the anil used, crystallization began either immediately on cooling, or after several hours, or after

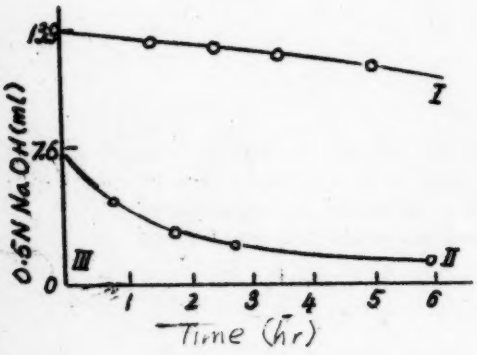


Fig. 1

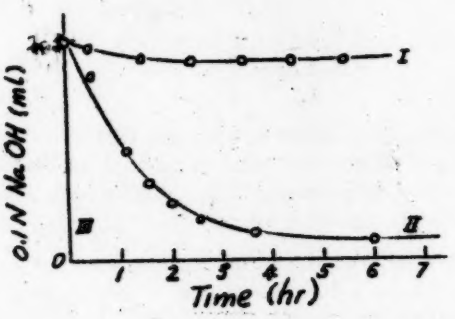


Fig. 2

several days. In a number of cases a crystalline product was not obtained even after a long period of standing. The crystalline products were filtered off, washed with cold alcohol, and recrystallized several times from hot ethanol until a constant melting point was obtained.

Addition of Dialkylphosphorous Acids to Acetophenone Anil and its Derivatives

A saturated solution of sodium alkoxide (25-25 drops was added to a mixture of the ketone anil (3-4 g) and an equimolecular amount of the dialkylphosphorous acid. In most of the experiments the reaction mixture did not

become warm. It was heated on a bath having a temperature of 150-180° for 1-2 hours, and was poured, after cooling, into a porcelain dish containing a few milliliters of alcohol. The crystalline products obtained were recrystallized from hot ethanol.

Kinetics of the Addition of Diethylphosphorous Acid to Benzylideneaniline

1. Diethylphosphorous acid in aqueous-alcoholic solution was titrated with 0.5 N NaOH in presence of phenolphthalein: 1 g of diethylphosphorous acid required 14.4 ml of 0.5 N NaOH (theory requires 14.5 ml). It was concluded that it was possible to determine the amount of unchanged diethylphosphorous acid present during the addition reaction by titration with caustic soda solution.

2. The procedure used in the kinetic studies was as follows: The benzylideneaniline was introduced into a 50-ml measuring flask, an equimolecular amount of diethylphosphorous acid was added, and absolute ethanol was added to a volume of 40-45 ml. The flask was placed in a thermostat, and after 30 minutes a solution of sodium methoxide was added, after which the contents of the flask were made up to volume by addition of absolute ethanol that had been heated in the thermostat. Analysis was carried out by transferring 5-ml portions to conical flasks containing a water-alcohol mixture; the unchanged diethylphosphorous acid was titrated rapidly with a 0.5 N or 0.1 N solution of NaOH. A "blank" experiment was carried out simultaneously. For illustration purposes we will give the results of one determination (Fig. 1). Benzylideneaniline, 13.1 g; diethylphosphorous acid, 10.0 g; 17.6% methanolic solution of sodium methoxide, 0.5, 1.0, and 3.0 ml. Temperature 50°. Blank experiment: 5 ml of solution required 13.9 ml of NaOH solution.

TABLE 4

No.	Time since beginning of expt.(hr)	0.5 N NaOH used in titration of diethylphosphorous acid (ml)		
		0.5 ml of catalyst	1.0 ml of catalyst	3 ml of catalyst
1	0	13.9	7.6	0
2	0.75	–	4.4	–
3	1.50	13.0	–	–
4	1.75	–	3.0	–
5	2.50	12.6	–	–
6	2.75	–	2.3	–
7	3.50	12.4	–	–
	5.00	9.5	–	–
	24.00	9.3	1.4	–

SUMMARY

A new method has been developed for the synthesis of amino phosphonics acids. It consists in the addition of dialkylphosphorous acids to anils in presence of alkali-metal alkoxides.

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LITERATURE CITED

[1] E. Knoevenagel, Ber. 37, 4081 (1907); P. Petrenko-Kritschenko, Ber. 42, 3683 (1909); E. Beckman, Ber. 23, 3340 (1890); R. Schiff, Ber. 31, 607, 206, 1390 (1898); K. Garzorolli, Ber. 32, 2277 (1899); M. Busch, Ber. 37, 2691 (1904).

[2] A. N. Pudovik, Proc. Acad. Sci. USSR., 73, 499, 327 (1950); 80, 65 (1951); Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci., No. 5, 522 (1951); J. Gen. Chem., 21, 383, 1837 (1951); A. N. Pudovik, ibid. 22, 462, 467, 473 (1952)* *

[3] A. N. Pudovik, Proc. Acad. Sci. USSR 83, 865 (1952).

[4] A. N. Pudovik, Proc. Acad. Sci. USSR 73, 327, 499 (1950).

* See Consultants Bureau translation, p. 423, 2035

** See Consultants Bureau translation, p. 525, 531, 537.

ADDITION OF DIALKYLPHOSPHOROUS ACIDS AND OF THEIR ACID CHLORIDES TO α-EPOXIDES

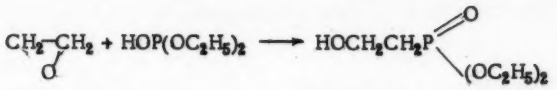
A. N. Pudovik and B. E. Ivanov

α-Epoxides form a class of very reactive organic compounds; they are capable of the most varied reactions: addition, replacement of oxygen, isomerization, and polymerization. Of these the most varied and interesting in theoretical and in practical respects are addition reactions. It has now been shown that α-epoxides are able to combine with the most varied substances: alcohols, phenols, water, organic acids and their acid chlorides, aldehydes and ketones, hydrogen halides, amino acids, malonic and acetoacetic esters, organomagnesium compounds, hydrogen sulfide and mercaptans, sulfuryl chloride, sulfuric chloride, and a number of others [1].

In connection with the work that one of us has been carrying out in recent years on the addition of dialkylphosphorous, dialkylphosphorothious, and alkyl- and aryl-phosphonous acids to unsaturated compounds [2] and of various nucleophilic reagents to vinylphosphonic esters [3], we considered it to be of interest and of importance to extend these investigations to a study of the addition of dialkylphosphorous acids, their analogs, and their acid chlorides to α-epoxides.

The addition of dialkylphosphorous acids to α-epoxides has remained practically without study until now. In the literature there is only a cursory reference to the possibility of such an addition by Chelintsev and Kuskova [4]: in the course of a reaction between ethylene oxide and sodium diethyl phosphite they obtained a syrup, in which the presence of quinquevalent phosphorus was established spectroscopically; no individual products were isolated from the mixture. We commenced our investigation by repeating Chelintsev and Kuskova's experiment. After passing ethylene oxide into an ethereal solution of sodium diethyl phosphite, treating the reaction mixture with acetic acid, filtering off sodium acetate, and distilling off the ether, we obtained a liquid similar in amount and appearance to that described by Chelintsev and Kuskova. However, vacuum fractionation indicated that it consisted essentially of diethylphosphorous acid and a small amount (several drops) of a fraction of b.p. 115-125°/5 mm; an appreciable amount of resinlike residue remained. Performance of the reaction at higher temperatures improved the yield of high-boiling fraction only slightly.

Petrov [5], in a study of the addition of alcohols to α-epoxides, has shown that a very effective catalyst in these reactions is boron trifluoride and its complexes with oxygen-containing compounds. It was of interest to examine the possibility of their application in the addition reactions of dialkylphosphorous acids, and we carried out experiments that indicated that they could be so applied: for the reaction between ethylene oxide and diethylphosphorous acid, the greatest yield (15-16%) of diethyl 2-hydroxyethylphosphonate was obtained when the reaction was carried out at 130-140° in presence of the ether complex (etherate) of boron trifluoride:



At lower temperatures (80-90°) the reaction does not go, and at higher temperatures (about 160°) the yield of addition product falls owing to formation of high-boiling fractions and resins. Addition to ethylene oxide of dimethylphosphorous acid proceeds in similar fashion, but we did not succeed in bringing about addition of dibutyl- and diisobutyl-phosphorous acids under our experimental conditions.

Since substituted α-epoxides are more reactive than ethylene oxide, we then carried out a series of experiments on the addition of diethylphosphorous acid to 1,2-epoxycyclohexane and to 1,2-epoxy-3-ethoxypropane in presence of boron trifluoride etherate; also of sodium diethyl phosphite to 1,2-epoxy-3-ethoxypropane. The addition product from 1,2-epoxycyclohexane (diethyl 2-hydroxycyclohexylphosphonate) was obtained in 20% yield. In the addition of diethylphosphorous acid to 1,2-epoxy-3-ethoxypropane, one or other of two different products, corres-

ponding by analysis and molecular-refraction results to the diethyl ester of ethoxyhydroxypropylphosphonic acid, were obtained according as catalyst was used or not. It is evident that, as in the case of the addition of alcohols [5], the catalyst has a determining effect on the direction of addition of dialkylphosphorous acids to α-epoxides. By analogy to the corresponding alcohol reactions, it may be supposed that addition of sodium dialkyl phosphite to 1,2-epoxy-3-ethoxypropane yields the normal addition product — diethyl 3-ethoxy-2-hydroxypropylphosphonate — whereas in presence of boron trifluoride reaction is abnormal and yields diethyl 2-ethoxy-2'-hydroxyisopropylphosphonate. In neither case does the yield of addition product exceed 20%.

Addition to α-epoxides of acid chlorides derived from partial phosphorous esters were studied by Kabachnik in a series of investigations [6]: he studied the addition of diphenyl phosphorochloridite, phenyl phosphorodichloridite, and o-phenylene phosphorochloridite to ethylene oxide. In the first case he isolated 2-chloroethyl diphenyl phosphite, which was converted, when strongly heated, into a tetraphenyl ethylenediphosphonate with loss of dichloroethane (2-chloroethyl o-phenylene phosphite behaved similarly).

Mixed phosphorous esters containing only aliphatic radicals were prepared by Kabachnik and Rosiiskaya [7] by Milobendzsky's reaction from Menshutkin's acid chloride. Thus, 2-chloroethyl diethyl phosphite was synthesized from the acid chloride $ClCH_2CH_2OPCl_2$ and alcohol in presence of pyridine, although the yield obtained by this reaction was only about 21%. Thermal isomerization of 2-chloroethyl diethyl phosphite yielded diethyl 2-chloroethylphosphonate.

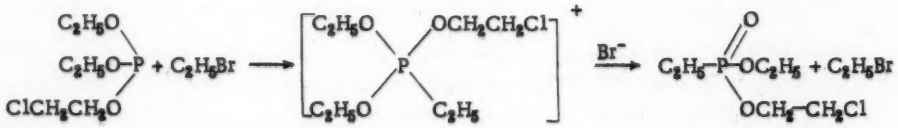
In view of the great theoretical interest afforded by mixed aliphatic esters of phosphorous acid, we decided to carry out their synthesis by the action of dialkyl phosphorochloridites on α-epoxides. Until recently, dialkyl phosphorochloridites have been inaccessible substances, but A. E. Arbuzov and coworkers have now developed a convenient method of synthesis consisting in the direct action of two molecular proportions of an alcohol on one molecular proportion of phosphorus trichloride in presence of dimethylaniline. In this way diethyl phosphorochloridite, ethylene phosphorochloridite, and a number of other cyclic phosphorochloridites have been synthesized [9]. The reaction between ethylene oxide and diethyl phosphorochloridite was very vigorous; it was carried out simply by passing gaseous ethylene oxide through the cooled phosphorochloridite. Fractionation of the reaction mixture yielded three products: 2-chloroethyl diethyl phosphite (51%), triethyl phosphite (13%), and bis(2-chloroethyl) ethyl phosphite (15%). The formation of triethyl phosphite and of bis(2-chloroethyl)ethyl phosphite can be explained by disproportionation of 2-chloroethyl diethyl phosphite during reaction:

$$(C_2H_5O)_2PCl + CH_2{-}CH_2 \longrightarrow (C_2H_5O)_2POCH_2CH_2Cl$$
$$\qquad\qquad\qquad\qquad\quad O$$

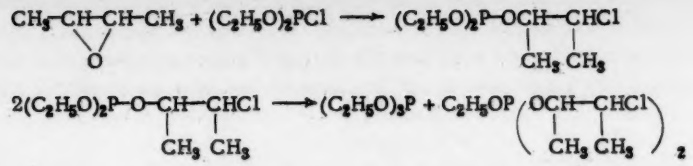
$$2(C_2H_5O)_2POCH_2CH_2Cl \longrightarrow (C_2H_5O)_3P + (C_2H_5O)P(OCH_2CH_2Cl)_2.$$

A similar phenomenon was observed by Kabachnik in the reaction between ethylene oxide and diphenyl phosphorochloridite [6].

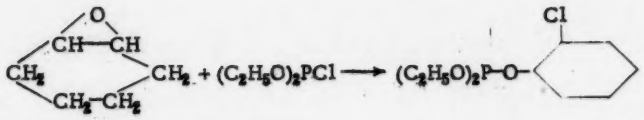
The constants of the products we have obtained are identical with those obtained for the same substances by Kabachnik. We subjected 2-chloroethyl diethyl phosphite to the isomerization reaction in presence of ethyl bromide: it was of interest to determine which of the radicals in the phosphorous ester — ethyl or 2-chloroethyl — would participate in the Arbuzov rearrangement. Experiment showed that the reaction went only in one direction, with formation of the isomerized product, 2-chloroethyl ethyl ethylphosphonate; an ethyl radical had therefore been split off.



We prepared 2,3-epoxybutane by oxidizing 2-butene with peroxyacetic acid in a dry ether medium, and its ethereal solution was applied directly in the reaction with diethyl phosphorochloridite (the reaction was carried out under cooling with ice water). Fractionation of the reaction mixture yielded three products: triethyl phosphite, 2-chloro-1-methylpropyl diethyl phosphite, and bis(2-chloro-1-methylpropyl)ethyl phosphite. The yield of 2-chloro-1-methylpropyl diethyl phosphite was 55%.

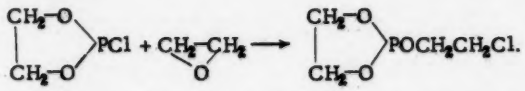


No tris(2-chloro-1-methylpropyl) phosphite was detected in the products. In the reaction between 1,2-epoxycyclohexene and diethyl phosphorochloridite, only one product was isolated: 2-chlorocyclohexyl diethyl phosphite (60%):



No high-boiling fractions were obtained.

Finally, we carried out the reaction between ethylene oxide and ethylene phosphorochloridite. The reaction was very vigorous, much heat being evolved. The only product was 2-chloroethyl ethylene phosphite, obtained in 95% yield:



The product had constants identical with those of the substance obtained by A. E. Arbuzov, Zoroastrova, and Rizpolozhensky by the action of 2-chloroethanol on ethylene phosphorochloridite in presence of pyridine.

EXPERIMENTAL

Addition of Diethylphosphorous Acid to Ethylene Oxide

Expt. 1. Finely cut sodium (1.7 g) was added to absolute ether (100 ml) contained in a flask provided with reflux condenser and dropping funnel, from which diethylphosphorous acid (10 g) was added. The mixture was allowed to stand, first at room temperature and then warm, on a water bath, until the sodium had completely dissolved. Gaseous ethylene oxide was passed through the solution until the weight had increased by 3.5 g, and then acetic acid (5.5 g) was added. The precipitate of sodium acetate was filtered off, and ether was distilled off on a water bath. The residue was fractionally distilled under 10 mm pressure, yielding:

Fraction I, b.p. 70-80°; 8 g (diethylphosphorous acid)
Fraction II, b.p. 80-110°; a few drops
Fraction III, b.p. 110-120°; a few drops

The residue in the flask was a resinous mass containing an appreciable amount of sodium acetate.

Expt. 2. An ethereal solution of sodium diethyl phosphite, obtained as in Expt. 1, was heated at 40° on a water bath, and ethylene oxide was passed until the increase in weight attained 3.5 g. After removal of precipitate and solvent, a syruplike mass was obtained, from which by fractionation under 5 mm pressure the following three fractions were obtained:

Fraction I, b.p. 60-70°; 6 g (diethylphosphorous acid)
Fraction II, b.p. 70-120°; 1 g
Fraction III, b.p. 120-130°; 1.5 g

Expt. 3. A small amount of sodium was dissolved in diethylphosphorous acid (5 g), ethylene oxide (5 g) was added, and the mixture was sealed in a tube and heated for five hours at 60°. Fractionation showed that the reaction had not gone. A similar experiment was carried out with the same amounts of reactants, but in presence of an alcoholic solution of sodium ethoxide (3 drops); however, vacuum fractionation yielded only the original substances.

Expt. 4. A mixture of diethylphosphorous acid (13.8 g), boron trifluoride etherate (0.1 ml), and ethylene oxide (6 g) was heated in a sealed tube at 85-90° for four hours. Fractionation of the reaction mixture yielded the

original substances and also a fraction (about 1 g) of b.p.130-150°/5 mm.

Expt. 5. A mixture of diethylphosphorous acid (20 g), boron trifluoride etherate (0.015 ml), and ethylene oxide (10 g) was heated in a sealed tube at 130° for 8 hours. Vacuum fractionation of the mixture yielded the following fractions:

Fraction I, b.p. 30-84° at 4.5 mm; 4 g
Fraction II, b.p. 60-70° at 4.5 mm; 8 g (diethylphosphorous acid)
Fraction III, b.p. 70-120° at 4.5 mm; 1 g
Fraction IV, b.p. 125-145° at 4.5 mm; 8 g

There was only a small amount of resinous residue in the flask. Refractionation of the fraction of b.p. 125-145°/4.5 mm yielded diethyl 2-hydroxyethylphosphonate, b.p. 122-124°/8 mm; n_D^{20} 1.4380; d_4^{20} 1.0927.

Found %: P 16.72
$C_6H_{15}O_4P$. Calculated %: P 17.02

Expt. 6. A mixture of diethylphosphorous acid (20 g), sulfuric acid (sp. gr. 1.8), and ethylene oxide (10 g) was heated at 130° for 8 hours. Fractionation of the mixture under 5 mm pressure yielded the following fractions:

Fraction I, b.p. 60-70°; 18 g (diethylphosphorous acid)
Fraction II, b.p. 70-115°; 2 g
Fraction III, b.p. 115-125°; 3 g n_D^{20} 1.4364

There was only a very small residue in the flask.

Addition of Dimethylphosphorous Acid to Ethylene Oxide

A mixture of dimethylphosphorous acid (20 g), boron trifluoride etherate (0.015 ml), and ethylene oxide (12 g) was heated in a sealed tube at 130-135° for 8 hours. Ethylene oxide was removed from the reaction mixture under suction, and vacuum fractionation then yielded 5 g of a fraction of b.p. 85-99°/6 mm. A residue of about 6 g remained in the flask. Refractionation yielded dimethyl 2-hydroxyethylphosphonate (3 g) having b.p. 95-97° at 6 mm; n_D^{20} 1.4240; d_4^{20} 1.1711; found MR_D 33.4; calculated MR_D 33.06.

Found %: P 19.83
$C_4H_{11}O_4P$. Calculated %: P 20.09

Addition of Diisobutyl- and Dibutyl-phosphorous Acids to Ethylene Oxide

Expt. 1. A mixture of dibutylphosphorous acid (10 g), ethylene oxide (6 g), and boron trifluoride etherate (0.015 ml) was heated at 130-135° for 8 hours. Fractionation of the reaction mixture yielded the original substances.

Expt. 2. A mixture of diisobutylphosphorous acid (15 g), ethylene oxide (7 g), and boron trifluoride etherate (0.015 ml) was heated at 130-135° for 8 hours. Fractionation of the reaction mixture showed that the reaction had not gone. Repetition of Expts. 1 and 2 at 160-170° again did not lead to positive results.

Addition of Diethylphosphorous Acid to 1,2-Epoxy-3-ethoxypropane

Expt. 1. Finely cut sodium (2.3 g) was added to absolute ether (100 ml), and diethylphosphorous acid (13.8 g) was added dropwise from a dropping funnel. The mixture was set aside until the sodium had completely dissolved. 1,2-epoxy-3-ethoxypropane (10.2 g) was added slowly to the ethereal solution obtained, and the reaction mixture was then heated on a water bath for three hours. Heating was discontinued, glacial acetic acid (7 g) was added, the precipitate of sodium acetate was filtered off, and the ether was driven off on a water bath. Vacuum fractionation of the residue at 5 mm yielded the following fractions:

Fraction I, b.p. 45-46°; 4 g
Fraction II, b.p. 65-115°; 0.7 g
Fraction III, b.p. 115-125°; 3.5 g

Refractionation of the fraction of b.p. 115-125°/5 mm yielded a product (1.7 g) of b.p. 115-116°/5 mm; d_4^{20} 1.0831; n_D^{20} 1.4385; found MR_D 58.1; calculated MR_D 57.8.

Found %: P 12.64
$C_9H_{21}O_5P$. Calculated %: P 12.92

Expt. 2. A mixture of diethylphosphorous acid (13.8 g), 1,2-epoxy-3-ethoxypropane (10.2 g), and boron trifluoride etherate (0.05 ml) was heated in a sealed tube at 130-135° for 8 hours. Fractionation of the reaction mixture under 5 mm pressure yielded the fractions:

Fraction I, b.p. 45-70°; 10 g
Fraction II, b.p. 70-130°; 0.8 g
Fraction III, b.p. 130-140°; 5 g
Fraction IV, b.p. 140-170°; 4.5 g

Refractionation of the fraction of b.p. 130-140°/5 mm yielded a substance (3 g) having b.p. 137-139° at 7 mm; d_4^{20} 1.1023; n_D^{20} 1.4432; found MR_D 57.64; calculated MR_D 57.8.

Found %: P 13.13; 13.07
$C_9H_{21}O_5P$. Calculated %: P 12.92

Refractionation of the fraction of b.p. 140-170°/5 mm yielded a fraction (2.5 g) having b.p. 155-156° at 7 mm; n_D^{20} 1.4520; d_4^{20} 1.1745.

Found %: P 14.88; 15.01

Addition of Diethylphosphorous Acid to 1,2-Epoxycyclohexane

A mixture of diethylphosphorous acid (25 g), 1,2-epoxycyclohexane (16 g), and boron trifluoride etherate (0.015 ml) was heated in a sealed tube at 140-150° for 8 hours. Vacuum fractionation of the reaction mixture yielded a fraction (7 g) of b.p. 140-150°/8 mm. Refractionation yielded diethyl 2-hydroxycylohexylphosphonate (4.5 g) having b.p. 142-144° at 8 mm; d_4^{20} 1.0930; n_D^{20} 1.4620; found MR_D 59.3; calculated MR_D 58.57.

Found %: P 13.09
$C_{10}H_{21}O_4P$. Calculated %: P 13.18

Addition of Diethyl Phosphorochloridite to Ethylene Oxide

Gaseous ethylene oxide was passed through diethyl phosphorochloridite (35 g) until there was an increase in weight of 10 g; the temperature of the reaction mixture was maintained in the range 20-25° by cooling the flask in ice water. Fractionation of the reaction mixture at 15 mm gave the following fractions:

Fraction I, b.p. 54- 58°; 7 g
Fraction II, b.p. 80- 89°; 25 g; n_D^{20} 1.4370
Fraction III, b.p. 89-125°; 2 g; n_D^{20} 1.4560
Fraction IV, b.p. 125-128°; 8 g; n_D^{20} 1.4609

Refractionation of Fraction I through a Widmer column yielded triethyl phosphite (4 g) of b.p. 46° at 7 mm; n_D^{20} 1.4138; d_4^{20} 0.9866. Refractionation of Fraction II yielded 2-chloroethyl diethyl phosphite (20 g) of b.p. 72-74° at 5 mm; n_D^{20} 1.4392; d_4^{20} 1.1038; found MR_D 47.89; calculated MR_D 47.84, (according to Kabachnik and Rossiiskaya, 2-chloroethyl diethyl phosphite has the constants: 71-72° at 5 mm; n_D^{20} 1.4391; d_4^{20} 1.1025. Our last fraction had constants (b.p. 125-128° at 15 mm; n_D^{20} 1.4609; d_4^{20} 1.2268) that corresponded to those of bis(2-chloroethyl)ethyl phosphite, also prepared by Kabachnik and Rossiiskaya (b.p. 111-113° at 6 mm; n_D^{20} 1.4617; d_4^{20} 1.2294).

Isomerization of 2-Chloroethyl Diethyl Phosphite.

A mixture of 2-chloroethyl diethyl phosphite (10 g) and ethyl bromide (5.5 g) was heated in a sealed tube for five hours at 160°. Vacuum fractionation yielded 2-chloroethyl ethyl ethylphosphonate (7 g) having b.p. 67-68° at 7 mm; d_4^{20} 1.0911; n_D^{20} 1.4168; found MR_D 46.19; calculated MR_D 45.64.

Found %: P15.69
$C_6H_{14}O_3ClP$. Calculated %: P 15.46

Addition of Diethyl Phosphorochloridite to 2,3-Epoxybutane

Diethyl phosphorochloridite (10 g) was added to a cooled ethereal solution of 2,3-epoxybutane. Excess of 2-butene and ether was removed under suction from a water pump, and the residue was fractionated under 12 mm through a Widmer column. Three fractions were isolated:

Fraction I, b.p. 54-56°; 3 g
Fraction II, b.p. 80-99°; 7.5 g
Fraction III, b.p. 135-140°; 4.5 g

Refractionation of Fraction I yielded triethyl phosphite (2.5 g) having b.p. 49-50° at 9 mm; n_D^{20} 1.4140. Refractionation of Fraction II yielded 2-chloro-1-methylpropyl diethyl phosphite (5 g) having b.p. 99° at 12 mm; n_D^{20} 1.4367; d_4^{20} 1.0633; found MR_D 56.3; calculated MR_D 57.08.

Found %: P 13.89

$C_8H_{18}O_3ClP$. Calculated %: P 13.57

Refractionation of Fraction III yielded bis(2-chloro-1-methylpropyl)ethyl phosphite (4 g) having b.p. 130-132° at 5 mm; n_D^{20} 1.4500; d_4^{20} 1.0931; found MR_D 71.54; calculated MR_D 71.18.

Found %: P 10.64; 10.37

$C_{10}H_{21}O_3Cl_2P$. Calculated %: P 10.65

Addition of Diethyl Phosphorochloridite to 1,2-Epoxycyclohexane

Diethyl phosphorochloridite (6.5 g) was added gradually to 1,2-epoxycyclohexane (4 g); the reaction mixture became very hot. Vacuum fractionation yielded a fraction (5 g) of b.p. 130-135°/17 mm, and from this, on refractionation, 2-chlorocyclohexyl diethyl phosphite (3 g) was obtained; it had b.p. 130-132° at 17 mm; n_D^{20} 1.4650; d_4^{20} 1.1082; found MR_D 63.38; calculated MR_D 64.11.

Found %: P 12.47

$C_{10}H_{20}O_3ClP$. Calculated %: P 12.18

Addition of Ethylene Phosphorochloridite to Ethylene oxide

Gaseous ethylene oxide was passed through cooled ethylene phosphorochloridite (15 g) until there was an increase in weight of 5.5 g. Fractionation through a Widmer column yielded 2-chloroethyl ethylene phosphite (19 g) having b.p. 82-83° at 10 mm; d_4^{20} 1.3185; n_D^{20} 1.4760. According to A.E. Arbuzov, Zoroastrova, and Rizpolozhensky it has the following constants: b.p. 78.5-79.5° at 6.5 mm; n_D^{20} 1.4755; d_0^{20} 1.3206.

SUMMARY

1. It has been shown that dimethylphosphorous and diethylphosphorous acids add to ethylene oxide, 1,2-epoxycyclohexane, and 1,2-epoxy-3-ethoxypropane in presence of small amounts of boron trifluoride etherate with formation of the corresponding esters of 2-hydroxyalkylphosphonic acids. When sulfuric acid or sodium diethyl phosphite is used as catalyst, the addition products are formed in low yield.

2. Diethyl and ethylene phosphorochloridites add readily to ethylene oxide, to 2,3-epoxybutane, and to 1,2-epoxycyclohexane. In the reaction between diethyl phosphorochloridite and ethylene oxide or 2,3-epoxybutane, the main product – 2-chloroethyl diethyl phosphite (or 2-chloro-1-methylpropyl diethyl phosphite) – was accompanied by by-products – triethyl phosphite and bis(2-chloroethyl) ethyl phosphite (or tris(2-chloro-1-methylpropyl)ethyl phosphite) – formed by a process of disproportionation during the reaction.

In the addition reactions between diethyl phosphorochloridite and 1,2-epoxycyclohexane and between ethylene phosphorochloridite and ethylene oxide, a single addition product was obtained in each case: 2-chlorocyclohexyl diethyl phosphite (66% yield) and 2-chloroethyl ethylene phosphite (95% yield).

LITERATURE CITED

[1] M. S. Malinovsky, Prog. Chem., 19, 576 (1950).

[2] A. N. Pudovik, Proc. Acad. Sci., U.S.S.R., 73, 327, 499 (1950); J. Gen. Chem. 21, 383, 1837 (1951); 22, 462, 467, 473 (1952). (See Consultants Bureau translation, J.Gen. Chem. p. 423, 2035 (1951); 525,531,537(1952)).

[3] A.N. Pudovik, Proc. Acad. Sci. U.S.S.R., 80, 65 (1951).

[4] V. V. Chelintsev and V. L. Kuskova, J. Gen. Chem., 9, 1481 (1946).

[5] A. A. Petrov, J. Gen. Chem., 10, 981 (1941); 14, 1038 (1944).

[6] M. I. Kabachnik, Bull. Acad. Sci., U.S.S.R., Div. Chem. Sci., 6, 631 (1947); M. I. Kabachnik and P.A. Rossiiskaya, Bull. Acad. Sci U.S.S.R. Div. Chem. Sci., 3, 295 (1946).

[7] M.I. Kabachnik and P.A. Rossiiskaya, Bull. Acad. Sci. U.S.S.R., 1, 95 (1948).

[8] T. Milobendzki, A. Sachnowski, C. 1918, 1. 1911.

[9] A.E. Arbuzov, V.M. Zoroastrova, and N.I. Rizpolozhensky, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 2, 209 (1948).

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ETHYLPHOSPHONOUS ESTERS AND SOME OF THEIR REACTIONS

COMMUNICATION 2. PARTIAL ESTERS OF ETHYLPHOSPHONOUS ACID

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On account of their interesting properties, partial esters of phosphorous acid (dialkylphosphorous acids) have been studied in some detail. Dialkylphosphorous acids now find wide application in the synthesis of organophosphorus compounds of various types: thus, their salts react with organic halides, yielding phosphonic esters [1], and, by the action of bromine on sodium diethyl phosphite, pyrophosphorous, hypophosphoric, and pyrophosphoric esters can be prepared [2].

It has been shown in our laboratory [3] that dialkylphosphorous acids will add at a double bond with formation of phosphonic esters, and Abramov [4] has shown that they will add at the carbonyl group of an unsaturated aldehyde or ketone with formation of α-hydroxy phosphonic esters.

Dialkylphosphorous acids have been applied recently in the preparation of compounds of practical importance, for example, insecticides. Also, considerable attention is being devoted to the study of the structure of dialkylphosphorous acids by physical methods [5].

Unlike dialkylphosphorous acids, partial esters of alkylphosphonous acids have not been described in the literature. In structure, they are very similar to dialkylphosphorous acids, and it is therefore of great interest to study their structure and properties both by chemical and by physical methods.

In a previous communication [6] we have described some full esters of ethylphosphonous acid and a few of their reactions. In the present paper we give results on the synthesis of partial esters of ethylphosphonous acid. Levitsky [7], and later Nylen [8], proposed a method for the synthesis of dialkylphosphorous acids consisting in the treatment of phosphorus trichloride with alcohols:

$$3ROH + PCl_3 = (RO)_2POH + 2HCl + RCl.$$

This method was applied by us to the synthesis of partial esters of ethylphosphonous acid, the now accessible ethylphosphonous dichloride being used as starting material:

$$C_2H_5PCl_2 + 2ROH = C_2H_5P(OR)(H)(=O) + HCl + RCl.$$

A number of esters were synthesized in this way; their properties are given in the table.

EXPERIMENTAL

Apparatus and Procedure. Alkyl hydrogen phosphonites were prepared in the Arbuzov flask itself: one of the necks of the flask was stoppered, and through the cork in the other neck passed a thermometer and a dropping funnel drawn out to a capillary reaching to the bottom of the flask. The alcohol was placed in the flask, and the calculated amount of ethylphosphonous dichloride in the funnel. The delivery tube on the flask was connected to the water pump, external cooling was applied, and ethylphosphonous dichloride was sucked through the capillary at such a rate that the temperature in the flask did not rise above 0°. When the whole of the calculated amount of the ethylphosphonous dichloride had been added, the flask was allowed to stand for a further 30 minutes in the cooling mixture. Cooling was then discontinued, and hydrogen chloride was drawn off (carbon dioxide was drawn in through the capillary). When the reaction products were fractionated, the temperature of the bath was raised slowly, so that the pressure did not rise above 25 mm.

1. Methyl Hydrogen Ethylphosphonite. The materials taken for reaction were ethylphosphonous dichloride (14 g) and methanol (10.5 g) (molar ratio of 1:3). Vacuum-fractionation of the reaction products yielded:

TABLE

No.	Formula	B.p. (°C)	Pressure (mm Hg)	d_4^{20}	n_D^{20}	MR_D		Yield (%)
						Calc.	Found	
1	$C_2H_5P(OCH_3)(OH)$	65-66	11	1.0796	1.4273	25.28	25.82	19.9
2	$C_2H_5P(OC_2H_5)(OH)$	68-69	9	1.0197	1.4242	29.90	30.52	31.0
3	$C_2H_5P(OC_3H_7\text{-}n)(OH)$	81-82	10	0.9937	1.4280	34.51	35.18	47.0
4	$C_2H_5P(OC_3H_7\text{-}i)(OH)$	69-70	10	0.9822	1.4233	34.51	35.34	42.0
5	$C_2H_5P(OC_4H_9\text{-}n)(OH)$	92-93	9	0.9759	1.4311	39.13	39.79	57.0
6	$C_2H_5P(OC_4H_9\text{-}i)(OH)$	86-87	9	0.9688	1.4300	39.13	40.00	56.5
7	$C_2H_5P(OC_6H_{13}\text{-}n)(OH)$	87-88	1.5	0.9511	1.4374	48.27	49.18	53.7
8	$C_2H_5P(OC_7H_{15}\text{-}n)(OH)$	99-100	4	0.9386	1.4395	52.89	54.02	42.0
9	$C_2H_5P(OC_8H_{17}\text{-}n)(OH)$	102-103	1	0.9320	1.4440	57.50	58.79	52.0
10	$C_2H_5P(OC_9H_{19}\text{-}n)(OH)$	122-123	4	0.9230	1.4431	62.12	63.32	59.0
11	$C_2H_5P(OC_{10}H_{21}\text{-}n)(OH)$	129-130	1.5	0.9296	1.4458	66.74	67.19	49.1

Frac. I, b.p. to 60° at 13-11 mm; 1.6 g
Frac. II, b.p. 60-68° at 11 mm; 4.6 g
The residue (4 g) was an almost colorless, viscous liquid.

Refractionation yielded methyl hydrogen ethylphosphonite (2.0 g, (19.9%) having the following constants: b.p. 65-66° at 11 mm; d_4^{20} 1.0796; n_D^{20} 1.4273; found MR_D 25.82; calculated for $C_3H_9O_2P$ MR_D 25.28.

Found %: P 28.52; 28.6
$C_3H_9O_2P$. Calculated %: P 28.85

Methyl hydrogen ethylphosphonite is a colorless, mobile, evil-smelling liquid.

2. Ethyl Hydrogen Ethylphosphonite. Ethylphosphonous dichloride (21.5 g) and ethanol (20.3 g) were taken for reaction. Fractionation of the reaction products yielded:

Frac. I, b.p. 40-80° at 25-11 mm; 16.5 g
The residue (8.5 g) was a colorless viscous liquid.

Refractionation yielded ethyl hydrogen ethylphosphonite (6.2 g, 31%) having the constants: b.p. 68-69° at 9 mm; d_4^{20} 1.0197; n_D^{20} 1.4242; found MR_D 30.52; calculated for $C_4H_{11}O_2P$, MR_D 29.90.

Found %: P 25.2; 25.31
$C_4H_{11}O_2P$. Calculated %: P 25.4

It is a colorless, mobile, evil-smelling liquid.

3. Propyl Hydrogen Ethylphosphonite. Ethylphosphonous dichloride (13 g) and propyl alcohol (17.8 g) were taken for reaction. Vacuum fractionation yielded:

Frac. I, b.p. to 76° at 20-15 mm; 2 g
Frac. II, b.p. 76-84° at 15-10 mm; 13 g
Residue 1.5 g

Refractionation yielded propyl hydrogen ethylphosphonite (5.8 g, 47%) having the following constants: b.p. 81-82° at 10 mm; d_4^{20} 0.9937; n_D^{20} 1.4280; found MR_D 35.18; calculated for $C_5H_{13}O_2P$, MR_D 34.51.

Found %: P 22.61; 22.60
$C_5H_{13}O_2P$. Calculated %: P 22.8

It is a colorless liquid having an unpleasant odor.

4. Isopropyl Hydrogen Ethylphosphonite. This was prepared from isopropyl alcohol (16.5 g) and ethylphosphonous dichloride (12 g). Fractionation yielded:

Frac. I, b.p. to 68° at 20-10 mm; 1.8 g
Frac. II, b.p. 69-73° at 10 mm; 10.5 g
Residue 1.6 g

Refractionation yielded isopropyl hydrogen ethylphosphonite (5.3 g, 42%) having the following constants: b.p. 69-70° at 10 mm; d_4^{20} 0.9822; n_D^{20} 1.4233; found MR_D 35.34; calculated for $C_5H_{13}O_2P$, MR_D 34.51.

Found %: P 22.6; 22.52
$C_5H_{13}O_2P$. Calculated %: P 22.8

It is a liquid having an unpleasant, phosphinelike odor.

5. Butyl Hydrogen Ethylphosphonite. This was prepared from ethylphosphonous dichloride (16 g) and butyl alcohol (27 g). Vacuum fractionation yielded:

Frac. I, b.p. 68-98° at 12-9 mm; 20 g
Residue 1.7 g

Refractionation yielded butyl hydrogen ethylphosphonite (10.5 g, 57%) having the following constants: b.p. 92-93° at 9 mm; d_4^{20} 0.9759; n_D^{20} 1.4311; found MR_D 39.79; calculated for $C_6H_{15}O_2P$, MR_D 39.13.

Found %: P 20.6; 20.65
$C_6H_{15}O_2P$. Calculated %: P 20.63

It is a colorless liquid of unpleasant phosphinelike odor, nonwetting to glass.

6. Isobutyl Hydrogen Ethylphosphonite. This was prepared from ethylphosphonous dichloride (8 g) and isobutyl alcohol (13 g). Fractionation of the reaction yielded:

Frac. I, b.p. to 85° at 20-10 mm; 3 g
Frac. II, b.p. 85-90° at 9 mm; 8.5 g
Residue 0.4 g

Refractionation yielded isobutyl hydrogen ethylphosphonite (5.2 g, 56.5%) having the following constants: b.p. 86-87° at 9 mm; d_4^{20} 0.9688; n_D^{20} 1.4300; found MR_D 40.00; calculated for $C_6H_{15}O_2P$, MR_D 39.13.

Found %: P 20.68; 20.52
$C_6H_{15}O_2P$. Calculated %: P 20.63

It is a colorless mobile liquid of unpleasant, phosphinelike odor.

7. Hexyl Hydrogen Ethylphosphonite. This was prepared from ethylphosphonous dichloride (8 g) and hexyl alcohol (19 g). Fractionation of the reaction products yielded:

Frac. I, b.p. to 117° at 15-9 mm
Frac. II, b.p. 65-87° at 1 mm; 10 g
Residue 1.2 g

Refractionation yielded hexyl hydrogen ethylphosphonite (5.8 g, 63.7%) having the following constants: b.p. 87-88° at 1.5 mm; d_4^{20} 0.9511; n_D^{20} 1.4374; found MR_D 49.18; calculated for $C_8H_{19}O_2P$, MR_D 48.27.

Found %: P 17.24; 17.3
$C_8H_{19}O_2P$. Calculated %: P 17.41

It is a mobile liquid of unpleasant phosphinelike odor; it is nonwetting to glass.

8. Heptyl Hydrogen Ethylphosphonite. This was prepared from ethylphosphonous dichloride (8.5 g) and heptyl alcohol (22.6 g). Vacuum distillation of the reaction products yielded:

Frac. I, b.p. 40-65° at 11 mm;
Frac. II, b.p. 54-96° at 4 mm;
Frac. III, b.p. 96-105° at 4 mm; 9.5 g
Residue 0.7 g

Refractionation yielded heptyl hydrogen ethylphosphonite (5.2 g, 42%) having the following constants: b.p. 99-100° at 4 mm; d_4^{20} 0.9386; n_D^{20} 1.4395; found MR_D 54.02; calculated for $C_9H_{21}O_2P$, MR_D 52.89.

Found %: P 15.85; 15.76
$C_9H_{21}O_2P$. Calculated %: P 16.12

It is a colorless mobile liquid of unpleasant, phosphinelike odor; it is nonwetting to glass.

9. Octyl Hydrogen Ethylphosphonite. This was prepared from ethylphosphonous dichloride (6.5 g) and octyl alcohol (16 g). Distillation of the reaction products yielded:

Frac. I, b.p. 63-70° at 9 mm
Frac. II, b.p. to 100° at 1.5 mm
Frac. III, b.p. 100-107° at 1.5 mm
Residue 0.6 g

Refractionation under reduced pressure yielded octyl hydrogen ethylphosphonite (5.3 g, 52.1%) having the following constants: b.p. 102-103° at 1 mm; d_4^{20} 0.9320; n_D^{20} 1.4440; found MR_D 58.79; calculated for $C_{10}H_{23}O_2P$. MR_D 57.50.

Found %: P 15.61; 15.55

$C_{10}H_{23}O_2P$. Calculated %: P 15.4

It is a colorless, mobile liquid of unpleasant odor.

10. Nonyl Hydrogen Ethylphosphonite. This was prepared from ethylphosphonous dichloride (11.5 g) and nonyl alcohol (25.5 g). Distillation of the reaction products yielded:

Frac. I, 64-120° at 3.5 mm;
Frac. II, 120-125° at 3.5 mm; 12 g
Residue 2.5 g

Refractionation yielded nonyl hydrogen ethylphosphonite (6.9 g, 59%) having the following constants: b.p. 122-123° at 4 mm; d_4^{20} 0.9230; n_D^{20} 1.4431; found MR_D 63.32; calculated for $C_{11}H_{25}O_2P$, MR_D 62.12.

Found %: P 13.78; 13.82

$C_{11}H_{25}O_2P$. Calculated %: P 14.08

It is a colorless, mobile, unpleasant-smelling liquid nonwetting to glass.

11. Decyl Hydrogen Ethylphosphonite. This was prepared from ethylphosphonous dichloride (9.3 g) and decyl alcohol (22.5 g). Distillation of the reaction products yielded:

Frac. I, b.p. 75-127° at 3 mm; 11.6 g
Frac. II, b.p. 127-129° at 3 mm;
Frac. III, b.p. 129-133° at 3 mm; } 11.2 g
Residue 1.7 g

Refractionation yielded decyl hydrogen ethylphosphonite (8.2 g, 49.1%) having the following constants: b.p. 129-130° at 1.5 mm; d_4^{20} 0.9296; n_D^{20} 1.4458; found MR_D 67.19; calculated for $C_{12}H_{27}O_2P$; MR_D 66.74.

Found %: P 13.4; 13.45

$C_{12}H_{27}O_2P$. Calculated %: P 13.22

It is a colorless mobile liquid of unpleasant odor.

SUMMARY

1. Partial esters of ethylphosphonous acid have been synthesized by the action of alcohols on ethylphosphonous dichloride.

2. Methyl, ethyl, propyl, isopropyl, butyl, isobutyl, hexyl, heptyl, octyl, nonyl, and decyl hydrogen ethylphosphonites have been prepared.

LITERATURE CITED

[1] M. Becker, Ber. 30, 1003 (1897). [2] A. E. Arbuzov and B. A. Arbuzov, J. Gen. Chem., 2, 371 (1932). [3] A. N. Pudovik and B. A. Arbuzov, Proc. Acad. Sci. U.S.S.R., 73, 2, 327 (1950); A.N. Pudovik and B.A. Arbuzov, J. Gen. Chem., 21, 383 (1951)*; A. N. Pudovik and B. A. Arbuzov, J. Gen. Chem., 21, 1837 (1951)** [4] V.S. Abramov, Proc. Acad. Sci. U.S.S.R. 73,3,487 (1950). [5] B.A. Arbuzov and V.S. Vinogradova, Proc. Acad. Sci., U.S.S.R., 54, 9, 795 (1946); B.A. Arbuzov and V. S. Vinogradova, Proc. Acad. Sci., U.S.S.R. 55, 1, 31 (1947); B.A. Arbuzov and V.S. Vinogradova, Proc. Acad. Sci. U.S.S.R. 72, 4, 695 (1950). [6] B.A. Arbuzov and N.I. Rizpolozhensky, Proc. Acad. Sci. U.S.S.R. 83, 4, 581 (1952). [7] N. Levitsky, J. Russ. Phys. Chem. Soc., 35, 215 (1903). [8] P. Nylen, Studien über organische Phosphorverbindungen, Upsala, 1930.

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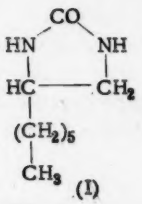
* See Consultants Bureau translation, p. 423.
** See Consultants Bureau translation, p. 2035.

THE CURTIUS REACTION IN THE β-AMINO ACID SERIES

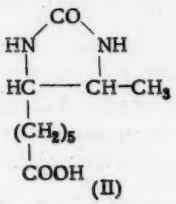
V. M. Rodionov and N. N. Bezinger

In the study of various reactions of β-amino acids, the readiness with which they are converted into various heterocyclic compounds is of great importance. In our laboratory we have now studied methods for the conversion of β-amino acids into tetra- and hexa-hydropyrimidines and into compounds of the imidazole series, and we have begun a study of syntheses of N-arylquinoline derivatives (via β-amino acids).

The conversion of β-amino acids into substituted imidazolidones is of exceptional interest, for preliminary investigations indicate that some of these compounds possess biotin activity. Thus, 4-hexyl-2-imidazolidone (I), which has been synthesized by Zvorykina [1], is very similar in structure to desthiobiotin (II) and, according to Meisel [2], differs very little from the latter in biological activity:

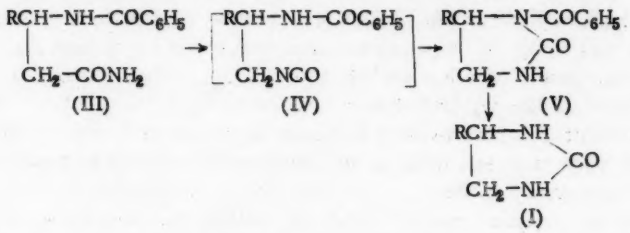


(I)



(II)

The hexylimidazolidone was prepared by the Hofmann reaction from β-benzamidopelargonamide and sodium hypobromite. The work of Zvorykina has afforded unequivocal evidence that for amides of acylated β-amino acids the Hofmann reaction proceed via the isocyanate, which undergoes intramolecular rearrangement with formation of imidazolidones containing an acyl group:



(III) (IV) (V) (I)

The mechanism of this reaction has been verified for a number of amides of acylated β-amino acids, and in all cases it has been confirmed by the isolation of acylated derivatives of imidazolidone (V) [3]. Whether these are isolated depends very much on the reaction temperature and on the amount of alkali. When the temperature is raised or the amount of alkali is increased, hydrolysis of (V) to give (I) is facilitated and no acylated imidazolidone can be isolated; this is what occurred in the older investigations on amides of β-amino acids.

Although this mechanism, which has been established for the formation of acyl derivatives of imidazolidone, was not in doubt, it was considered, nevertheless, that it would be very interesting to synthesize these compounds by an application of the Curtius reaction, for in that case the preparation of the isocyanates could be carried out via isolable azides. When acylamido azides are heated in an organic solvent in absence of alkali, the splitting off of the acyl group cannot occur, and the yield of acylated imidazolidones should be considerably greater than in the Hofmann reaction, which is carried out in an alkaline medium, i.e., with inevitable partial or complete splitting off of the acyl group. This supposition was fully justified, and a method has been developed for the synthesis of acylated imidazolidones.

We decided to investigate the following substances: N-benzoyl-β-phenyl-β-alanine, N-benzoyl-β-(m-nitrophenyl)-β-alanine, and N-benzoyl-β-piperonyl-β-alanine. As is well known, the Curtius reaction proceeds through

the following stages: hydrazide, azide, isocyanate, and the corresponding amine. In our case the isocyanate formed underwent intramolecular rearrangement and was converted into an acylated imidazolidone:

$$RCH(NHCOC_6H_5)CH_2-COOC_2H_5 \xrightarrow{H_2NNH_2} RCH(NHCOC_6H_5)CH_2-CONHNH_2 \xrightarrow{HONO} RCH(NHCOC_6H_5)CH_2CON_3 \rightarrow$$

$$\rightarrow RCH(NHCOC_6H_5)CH_2-NCO \rightarrow \begin{matrix} RCH-NCOC_6H_5 \\ | \quad\quad \diagdown CO \\ CH_2-NH \end{matrix}$$

The hydrazides were prepared from esters of N-benzoylated β-amino acids. The esters were boiled with a small excess of hydrazine hydrate, yielding hydrazides in 70-80% yield. The ester of N-benzoyl-β-piperonyl-β-alanine was an exception: it was found necessary to add a three-fold excess of hydrazine hydrate in this case, for otherwise the reaction did not go and the ester was isolated unchanged. An interesting observation was made when the ester of N-benzoyl-β-(m-nitrophenyl)-β-alanine was treated with a large excess of hydrazine hydrate: reaction occurred with simultaneous reduction of the nitro group and formation in good yield of the hydrazide of β-(m-aminophenyl)-N-benzoyl-β-alanine.

Two methods were tried for the preparation of azides: via the hydrazide, which was treated with oxides of nitrogen or nitrite, and by condensation of the acid chloride with sodium azide. The first method was preferred, for the azides were prepared via hydrazides in 90-95% yield and could be readily isolated in the pure state. The condensation of the acid chlorides was very slow, and very variable yields were obtained: it is possible that the lack of success was due to the use of insufficiently pure sodium azide.

When attempts were made to convert the azides into urethans, it was found that only the azide of N-benzoyl-β-phenyl-β-alanine was converted into the corresponding urethan when heated with absolute alcohol. The azides of N-benzoyl-β-(m-nitrophenyl)-β-alanine and of N-benzoyl-β-piperonyl-β-alanine did not form urethans; cyclization occurred with formation of 4-aryl-3-benzoyl-2-imidazolidones. Formationof the imidazolidone derivative generally occurred quantitatively.

The three azides all form imidazolidone derivatives when heated in dry benzene. Ring closure goes so readily in the case of N-benzoyl-β-(m-nitrophenyl)-β-alanine and N-benzoyl-β-piperonyl-β-alanine that, on being boiled with absolute alcohol, they form not the corresponding urethans, but imidazolidone derivatives.

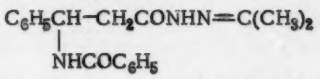
When 4-aryl-3-benzoyl-2-imidazolidones are hydrolyzed with hydrochloric acid, the ring is readily broken with evolution of carbon dioxide, splitting off of benzoic acid, and formation of the corresponding 1-arylethylenediamine. When hydrolysis is carried out with 10% caustic alkali at 80°, the benzoyl group is split off very readily, and a 4-aryl-2-imidazolidone is formed. It should be noted that in the free N-benzoyl β-amino acids, and also in their hydrazides, the benzoyl group is bound very firmly. Thus, when the hydrazides of N-benzoyl-β-phenyl-β-alanine and N-benzoyl-β-(m-nitrophenyl)-β-alanine are heated for many hours with a 10% solution of caustic alkali, the benzoyl groups are not split off. The position is similar, as already indicated, for the amides of N-benzoylated β-amino acids. We have found, therefore, that, in the Curtius rearrangement of azides of N-benzoylated β-amino acids, there are formed under our conditions five-membered cycles (imidazolidone derivatives) instead of isocyanates. The cyclization occurs extremely readily – simply by heating in an anhydrous solvent (benzene or absolute alcohol).

EXPERIMENTAL

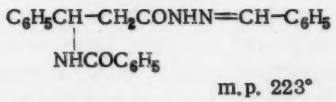
Hydrazide of N-Benzoyl-β-phenyl-β-alanine. The ethyl ester of N-benzoyl-β-phenyl-β-alanine [4] was dissolved in 80% alcohol (100 ml), and the solution was introduced into a two-necked flask provided with reflux condenser and dropping funnel. The flask was immersed in a water bath, and the contents were heated to the boil. A solution of hydrazine hydrate (3.5 g) in water (10 ml) was added dropwise to the boiling solution, and, when the addition was complete, the reaction mixture was heated on the water bath for a further four hours. When the solution was cooled, white silky crystals of N-benzoyl-β-phenyl-β-alanine hydrazide came down; they were filtered off under suction, washed with water and then alcohol, and dried. About one half of the alcohol present was distilled off from the mother liquor, which, on cooling, yielded a further crop of hydrazide. Recrystallization from ethanol yielded 11.7 g (82% of the ester taken for reaction) of N-benzoyl-β-phenyl-β-alanine hydrazine, b.p. 212-213°.

	Found %:	C 67.70; 67.73;	H 5.59; 5.62;	N 14.92; 14.70
$C_{16}H_{17}O_2N_3$.	Calculated %:	C 67.82;	H 5.69;	N 14.84

N-Benzoyl-β-phenyl-β-alanine hydrazide reduces an ammoniacal solution of silver in the cold, and Fehling's solution on being warmed. On being heated with acetone or with an alcoholic solution of benzaldehyde, it gives a high-melting condensation product, respectively:



m.p. 221°



m.p. 223°

N-benzoyl-β-phenyl-β-alanine hydrazide is a difficultly soluble substance, and its low solubility makes its conversion into the azide by the usual method difficult. It was thought that its hydrochloride would have a higher solubility, and an attempt was made to prepare it.

The Hydrochloride of N-Benzoyl-β-phenyl-β-alanine hydrazide. N-Benzoyl-β-phenyl-β-alanine hydrazide (4 g) was ground in a mortar with concentrated HCl (6 ml; sp. gr. 1.19). The slurry was set aside for several days in a desiccator over H_2SO_4 and alkali. The hydrochloride of N-benzoyl-β-phenyl-β-alanine was recrystallized from alcohol (4.3 g, 95.5%; m.p. 240°). The hydrochloride dissolved readily in alcohol and in hot water, but when its aqueous solutions were cooled it was almost completely precipitated, so that these solutions were not suitable for the preparation of the azide.

	Found %:	C 59.96; 60.11;	H 5.34; 5.34;	N 13.00; 13.05
$C_{16}H_{15}O_2N_3Cl$	Calculated %:	C 60.07;	H 5.67;	N 13.15

N-Benzoyl-β-phenyl-β-alanyl Azide. The azide was prepared by two methods: from the hydrazide, and from N-benzoyl-β-phenyl-β-alanyl chloride.

a) Preparation of N-benzoyl-β-phenyl-β-alanyl azide from the hydrazide. Of the known methods of converting hydrazides into azides, the most convenient appeared to us to be gaseous-N_2O_3 treatment. As already mentioned, the hydrazide of N-benzoy-β-phenyl-β-alanine is difficultly soluble generally, and particularly so in water, even when acidified. The dissolution of a few grams of hydrazide requires a very large volume of water, with which it is difficult to work. The necessary N_2O_3 was obtained by addition of HNO_3 to starch.

N-benzoyl-β-phenyl-β-alanine hydrazide (5 g) was carefully ground with water (70 ml) in a mortar, and the slurry obtained was transferred to an Erlenmeyer flask, which was immersed in an ice bath. When the temperature of the slurry had reached 0°, a uniform stream of N_2O_3 (more correctly, an equimolecular mixture of NO and NO_2) was passed, care being taken that the reaction temperature did not rise above +3°. The mixture was stirred constantly and vigorously. The reaction was complete in 15-25 minutes, and it was found possible to determine accurately when the reaction was complete by a characteristic change in the appearance of the precipitate: at first this formed a homogenous mass, but towards the end of the reaction it formed into lumps and acquired a sticky appearance. When reaction was complete the azide of N-benzoyl-β-phenyl-β-alanine was extracted with ether, when all the solids present generally went into solution: if some remained undissolved, this indicated that not all of the hydrazide had reacted, in which case it could be collected and used again.

The ethereal solution of the azide was washed several times with a 3% solution of $NaHCO_3$ and then with water. It was then dried with $CaCl_2$, filtered from the $CaCl_2$, and transferred to a vessel having two side tubes. The vessel was firmly stoppered and placed in a water bath at 23-25°. A stream of dry air (dried by passage through concentrated H_2SO_4) was then passed through the solution. When the whole of the ether had evaporated, a white powder, N-benzoyl-β-phenyl-β-alanyl azide, remained in the vessel.

The azide was recrystallized from dry chloroform by dissolving it in the cold, and then partially evaporating off the solvent. The glistening crystals (4.9 g, 93.4%) that formed decomposed at 74°. N-Benzoyl-β-phenyl-β-alanyl azide dissolves readily in the cold in alcohol, ether and chloroform.

b) Preparation of N-benzoyl-β-phenyl-β-alanyl azide from N-benzoyl-β-phenyl-β-alanyl chloride and NaN_3. Dry N-benzoyl-β-phenyl-β-alanine (5 g) was heated with excess (4 ml) of thionyl chloride in a flask fitted with reflux condenser and immersed in a water bath at 40-43°. Heating was continued until bubbles of HCl ceased to be evolved from the reaction mixture (three hours), and then for a further hour (four hours in all). The excess of

thionyl chloride was driven off under reduced pressure, and a brown viscous mass of pungent odor remained in the flask. On being rubbed out with absolute ether, it crystallized, forming a pale-yellow powder. N-benzoyl-β-phenyl-β-alanyl chloride was not investigated further owing to the difficulty of purifying it. Only the melting point of the impure product was determined; it was 166-168°.

The N-benzoyl-β-phenyl-β-alanyl chloride that had been prepared was transferred to an Erlenmeyer flask, and ether was added to bring the total volume to 150 ml. NaN_3 (1.4 g, i.e., 1.17 mole) was added, and the mixture was shaken mechanically for 50 hours. The ethereal solution was then separated from the precipitate, which consisted of unchanged acid chloride, NaN_3, and NaCl, and was evaporated in a stream of dry air (the vessel containing the ethereal solution was immersed in a water bath at 23-25°). The residue that remained in the vessel when the whole of the ether had been evaporated was a yellowish powder, identical in properties with the azide obtained from the hydrazide. The yield was 1.6 g (29.2% of the N-benzoyl-β-phenyl-β-alanine). Its decomposition temperature was 74°.

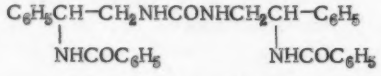
Conversion of N-Benzoyl-β-phenyl-β-alanyl Azide into the Urethan. Absolute alcohol (50 ml) was added to N-benzoyl-β-phenyl-β-alanyl azide (2 g), contained in a flask fitted with reflux condenser, and the mixture was heated on a boiling water bath for three hours. During this time there was vigorous evolution of gas (nitrogen). When reaction was complete, the solution was evaporated to dryness. A light-brown oil, which rapidly crystallized, when cooled and rubbed out, remained in the dish. The product, the ethyl ester of 2-benzamido-2-phenylethyl-carbamic acid, was recrystallized from aqueous alcohol; the yield was 1.68 g (78%). The urethan melts at 163.5° and is soluble in alcohol, chloroform, acetone, and acetic acid.

	Found %:	C 69.39; 69.20;	H 6.14; 6.17;	N 8.93; 8.82
$C_{18}H_{20}O_3N_2$.	Calculated %:	C 69.22;	H 6.45;	N 8.97

Preparation of 3-Benzoyl-4-phenyl-2-imidazolidone from N-Benzoyl-β-phenyl-β-alanyl Azide. N-benzoyl-α-phenyl-β-alanyl azide (5.2 g) was placed in a flask, and absolute benzene (80 ml) was added. The mixture was maintained at the boil on a water bath; there was vigorous evolution of nitrogen. When nitrogen evolution had ceased, heating was continued for a further one hour (90 minutes altogether). The solution was cooled, and the 3-benzoyl-4-phenyl-2-imidazolidone that precipitated was filtered off and crystallized from ethanol (fine glistening needles).

	Found %:	C 72.20; 72.04;	H 5.37; 5.50;	N 10.63; 10.66
$C_{16}H_{14}O_2N_2$.	Calculated %:	C 72.16;	H 5.30;	N 10.52

Hydrolysis of 3-Benzoyl-4-phenyl-2-imidazolidone with 10% KOH. 3-Benzoyl-4-phenyl-2-imidazolidone (2.7 g) was mixed with 10% KOH solution (20 ml) and heated at 80° on the water bath for 90 minutes. The reaction mixture always contained solid material, and when heating was discontinued this was filtered off from the hot solution, washed with water and then alcohol, and dried. Recrystallization from 96% alcohol gave a light product that resembled cotton wool (0.7 g; m.p. 239.5°). Analysis indicated that the substance was probably a symmetrically dialkylated urea derivative, but it was not examined further:



	Found %:	C 73.54; 73.36;	H 5.91; 6.10;	N 11.16; 11.15
$C_{31}H_{30}O_3N_4$.	Calculated %:	C 73.94;	H 5.97;	N 11.06

When the alkaline filtrate was cooled, a substance separated in the form of glistening plates; it was filtered off, washed with water and then alcohol, and dried. Recrystallization from ethanol yielded a substance (0.2 g) of m.p. 162-163°. In admixture with 4-phenyl-2-imidazolidone it showed no depression of melting point.

Preparation of N-Benzoyl-β-(m-nitrophenyl)-β-alanine. β-(m-Nitrophenyl)-β-alanine (31 g) was dissolved in a 10% NaOH solution (120 ml), and the solution obtained was cooled to 0°. The solution was stirred, and benzoyl chloride (15.4 g) was added dropwise, care being taken that the temperature of the solution did not rise above +10°. When the whole of the benzoyl chloride had been added, stirring was continued for a further one hour. The solution was then acidified with HCl (1:3) until acid to Congo red. A viscous mass of N-benzoyl-β-(m-nitrophenyl)-β-alanine was precipitated. It crystallized fairly quickly and was removed from the solution, ground up, and boiled several times with water (70-100 ml) to remove the greater part of the benzoic acid present. Recrystallization from methanol gave N-benzoyl-β-(m-nitrophenyl)-β-alanine (24.5 g, i.e. 78%, based on the amount of amino acid taken for reaction) of m.p. 204-205°.

Found %: N 8.98; 8.90

$C_{16}H_{14}O_5N_2$. Calculated %: N 8.91

Preparation of the Ethyl Ester of N-Benzoyl-β-(m-nitrophenyl)-β-alanine. Concentrated H_2SO_4 (12 ml) was added cautiously to 96% ethanol (200 ml), and then N-benzoyl-β-(m-nitrophenyl)-β-alanine (21 g) was added. The mixture, contained in a flask fitted with reflux condenser, was heated on a water bath for seven hours. The whole of the N-benzoyl-β-(m-nitrophenyl)-β-alanine went into solution almost immediately. When reaction was complete, the solution was cooled and the ethyl ester of N-benzoyl-β-(m-nitrophenyl)-β-alanine came down in the form of large clear needles. It was filtered off under suction, washed with a small amount of cooled alcohol, and dried. To the stirred cooled filtrate an equal volume of water was added, and a further amount of the ester came down. It was crystallized for analysis from 70% ethanol; it had m.p. 110-110.5°. The yield was 21.0 g (92% of the N-benzoyl-β-(m-nitrophenyl)-β-alanine).

Found %: N 8.36; 8.20

$C_{18}H_{18}O_5N_2$. Calculated %: N 8.18

Preparation of N-Benzoyl-β-(m-nitrophenyl)-β-alanine Hydrazide. N-Benzoyl-β-(m-nitrophenyl)-β-alanine hydrazide was prepared by heating the ethyl ester of N-benzoyl-β-(m-nitrophenyl)-β-alanine with a slight excess of hydrazine hydrate in 70% ethanol. If the reaction is carried out in 96% ethanol with a small excess of hydrazine hydrate, the yield of hydrazide is appreciably reduced (from 70-74% to 42%). When a large excess of hydrazine hydrate is used, simultaneous reduction of the NO_2 group occurs and a mixture is obtained of the hydrazides of N-benzoyl-β-(m-nitrophenyl)-β-alanine and of β-(m-aminophenyl)-N-benzoyl-β-alanine, which cannot be separated readily by simple recrystallization.

If the reaction is carried out without solvent by heating a mixture of hydrazine hydrate (in excess) with the ethyl ester of N-benzoyl-β-(m-nitrophenyl)-β-alanine, then the hydrazide of β-(m-aminophenyl)-N-benzoyl-β-alanine is the sole product.

The ethyl ester of N-benzoyl-β-(m-nitrophenyl)-β-alanine (17.1 g; 0.05 mole) was dissolved by heat in 70% ethanol (200 ml), and hydrazine hydrate (4 g; 0.08 mole) was added. The mixture, contained in a flask fitted with reflux condenser, was heated on a boiling water bath for five hours. When the solution was cooled, the hydrazide came out in a form resembling cotton wool; it was filtered off under suction, washed with alcohol, and dried. About half of the alcohol was distilled off from the filtrate, which then, when cooled, yielded a further crop of hydrazide. N-Benzoyl-β-(m-nitrophenyl)-β-alanine hydrazide [11.5 g, equivalent to 70% of the ethyl ester of N-benzoyl-β-(m-nitrophenyl)-β-alanine taken] maybe recrystallized from ethanol or methanol; m.p. 226-227°.

Found %: C 58.27; 58.75; H 4.72; 5.14; N 17.06; 16.94

$C_{16}H_{16}O_4N_4$. Calculated %: C 58.52; H 4.92; N 17.06

N-Benzoyl-β-(m-nitrophenyl)-β-alanine hydrazide is readily soluble in acids (CH_3COOH, HCl) and, when heated, in alcohol; it is completely insoluble in water. It readily reduces hot ammoniacal silver oxide and Fehling's solution.

Preparation of β-(m-aminophenyl)-N-benzoyl-β-alanine Hydrazide. Hydrazine hydrate (4.5 g; 0.09 mole) was placed in an Erlenmeyer flask fitted with reflux condenser and brought to the boil. The ethyl ester of N-benzoyl-β-(m-nitrophenyl)-β-alanine (3.4 g), was added in small portions, each portion being allowed to dissolve completely before the next was added. When the whole of the ester had been added, the solution was boiled for a further two hours and then cooled, when it formed a thick yellowish slurry. The precipitate was filtered off under suction, washed many times on the filter with water, and dried. Recrystallization from ethanol gave β-(m-aminophenyl)-N-benzoyl-β-alanine hydrazide, m.p. 205°, yield 2 g (67.2% of ethyl ester of N-benzoyl-β-(m-nitrophenyl)-β-alanine taken).

Found %: C 67.56; 67.40; H 6.10; 6.12; N 18.84; 18.72

$C_{16}H_{18}O_2N_4$. Calculated %: C 67.45; H 6.08 N 18.78

Preparation of N-Benzoyl-β-(m-nitrophenyl)-β-alanyl Azide. Water (400 ml) was added to N-benzoyl-β-(m-nitrophenyl)-β-alanine hydrazide (2 g), and the mixture was brought to the boil. The greater part of the hydrazide dissolved, and the remainder dissolved when concentrated HCl (20 ml) was added to the hot solution. The solution was cooled, suspended matter was filtered off, and the filtrate was placed in an ice bath. When the temperature of the solution had fallen to 0°, it was stirred vigorously while a solution of $NaNO_2$ (0.42 g) in water (5 ml) was added rapidly. A white flocculent precipitate came down immediately; it was rapidly filtered off under suction, washed on the filter with cold water, carefully pressed out on a porous tile, and dried in a vacuum desiccator over concentrated H_2SO_4.

N-Benzoyl-β-(m-nitrophenyl)-β-alanyl azide was recrystallized from chloroform by dissolving it in the cold and evaporating off the solvent. A small amount of crystals and a sirupy liquid remained in the dish, and to remove solvent completely the dish was placed in a vacuum desiccator for 1-2 hours. N-Benzoyl-β-(m-nitrophenyl)-β-alanyl azide remained behind in the form of glistening yellowish crystals, which decomposed at 60°. The yield of azide varied from 90 to 95% (of the equivalent of hydrazide taken).

An attempt to extract N-benzoyl-β-(m-nitrophenyl)-β-alanyl azide from the mixture obtained after addition of $NaNO_2$ by means of ether or chloroform did not lead to the required result. The azide is fairly soluble in these solvents, but it was not found possible to recover it from its solutions as such: during the standing of the solution over $CaCl_2$, splitting off of nitrogen evidently occurred with rearrangement of the azide into 3-benzoyl-4-(m-nitrophenyl)-2-imidazolidone.

Preparation of 3-Benzoyl-4-(m-nitrophenyl)-2-imidazolidone. N-Benzoyl-β-(m-nitrophenyl)-β-alanyl azide (2 g) was boiled with dry benzene (75 ml) in a flask fitted with reflux condenser. At first the azide formed into a viscous mass and floated on the surface of the benzene. Vigorous evolution of nitrogen occurred, and the viscous mass gradually resolidified, thus giving an indication of the end of the reaction. Heating was continued for a further thirty minutes (two hours altogether), the solution was cooled, and the 3-benzoyl-4-(m-nitrophenyl)-2-imidazolidone was filtered off. Recrystallization from a mixture of ethanol (five parts) and acetic acid (one part) gave fine glistening leaflike crystals (1.75 g, 96%), m.p. 233.5-234.5°.

Found %: C 61.50; 61.68; H 4.26; 4.31; N 31.51; 13.45
$C_{16}H_{13}O_4N_3$. Calculated %: C 61.72; H 4.21 N 13.49

3-Benzoyl-4-(m-nitrophenyl)-2-imidazolidone may be prepared by boiling the azide with water or alcohol. Even when the azide is boiled with absolute alcohol, the product is not the expected urethan, but 3-benzoyl-4-(m-nitrophenyl)-2-imidazolidone in 85-90% yield.

Preparation of 4-(m-nitrophenyl)-2-imidazolidone. 3-Benzoyl-4-(m-nitrophenyl)-2-imidazolidone (2 g) was mixed with 10% KOH solution (50 ml), and the mixture was heated in a flask at 80-85° on a water bath for one hour. Towards the end of this period the 3-benzoyl-4-(m-nitrophenyl)-2-imidazolidone went completely into solution. The solution was filtered hot to remove suspended matter, and was then cooled. 4-(m-Nitrophenyl)-2-imidazolidone came out in the form of a yellow powder: it was filtered off, washed with water, dried, and recrystallized from methanol. It melted at 179°.

Found %: C 52.21; 52.25; H 4.45; 4.42; N 20.40; 20.40
$C_9H_9O_3N_3$. Calculated %: C 52.17; H 4.38; N 20.32

Acidification of the alkaline filtrate with HCl (1:3) yielded benzoic acid (0.7 g).

Preparation of the Ethyl Ester of N-Benzoyl-β-piperonyl-β-alanine. N-Benzoyl-β-piperonyl-β-alanine (10 g) was dissolved in 96% ethanol, and concentrated sulfuric acid (6 ml) was added. The mixture, contained in a flask fitted with reflux condenser, was heated on a boiling water bath for seven hours. The solution was then cooled, and an equal volume of water was added. N-Benzoyl-β-piperonyl-β-alanine ethyl ester separated as a yellow mass, which crystallized almost instantaneously. It was filtered off and recrystallized from 50% ethanol (m.p. 130.5-131°). The yield was 8.95 g (82% of N-benzoyl-β-piperonyl-β-alanine taken).

Found %: N 4.26; 4.08
$C_{19}H_{19}O_5N$. Calculated %: N 4.10

Preparation of N-Benzoyl-β-piperonyl-β-alanine Hydrazide. N-Benzoyl-β-piperonyl-β-alanine ethyl ester (8 g) was dissolved by heat in 96% alcohol (100 ml), and hydrazine hydrate (3.57 g a three-fold excess) was added. The mixture, contained in a flask fitted with reflux condenser, was heated on a water bath for eight hours. When the solution was cooled, N-benzoyl-β-piperonyl-β-alanine hydrazide came down as glistening needles: it was filtered off, washed with alcohol, and dried. About two-thirds of the alcohol in the filtrate was evaporated, and by cooling the solution a further crop of the hydrazide was then obtained. N-Benzoyl-β-piperonyl-β-alanine hydrazide was recrystallized from ethanol (m.p. 224-225°). The yield was 6.9 g (90% of the ester taken for reaction).

Found %: C 62.61; 62.34; H 5.21; 5.17; N 12.91; 12.83.
$C_{17}H_{17}O_4N_3$. Calculated %: C 62.37; H 5.25; N 12.84.

N-Benzoyl-β-piperonyl-β-alanine hydrazide reduces ammoniacal silver oxide in the cold, and Fehling's solution when heated.

Preparation of N-Benzoyl-β-piperonyl-β-alanyl Azide. Boiling water (400 ml) and concentrated HCl (15 ml) were added to N-benzoyl-β-piperonyl-β-alanine hydrazide (5 g). The solution was cooled to room temperature, suspended matter present was filtered off, and the solution was cooled further to 0°. A solution of $NaNO_2$ (1.1 g) in water (5 ml) was then added rapidly under vigorous stirring. N-Benzoyl-β-piperonyl-β-alanyl azide was precipitated immediately in the form of compact white flakes: it was rapidly filtered off under suction, washed with ice water, and dried – first on a porous tile, and then in a vacuum desiccator. It decomposed at 50-51°. The yield was 4.38 g (85% of the hydrazide taken).

Preparation of 3-Benzoyl-4-piperonyl-2-imidazolidone. N-Benzoyl-β-piperonyl-β-alanyl azide (2 g) in absolute benzene (80 ml) contained in a flask fitted with reflux condenser was heated on a water bath at the boiling point of benzene. Vigorous evolution of nitrogen began at a bath temperature of about 60°, and heating was continued until evolution of nitrogen ceased (90 minutes). The solution was cooled, and the precipitated 3-benzoyl-4-piperonyl-2-imidazolidone was filtered off. It was recrystallized from butyl alcohol (m.p. 241°). The yield was 1.8 g (98%).

	Found %: C 65.86; 65.91;	H 4.65; 4.50;	N 9.10; 8.96
$C_{17}H_{14}O_4N_2$.	Calculated %: C 65.80;	H 4.55;	N 9.04

3-Benzoyl-4-piperonyl-2-imidazolidone is formed also when N-benzoyl-β-piperonyl-β-alanyl azide is heated with water (35-40% yield), and also when it is heated with alcohol.

Hydrolysis of 3-Benzoyl-4-piperonyl-2-imidazolidone with 10% KOH Solution. 3-Benzoyl-4-piperonyl-2-imidazolidone (2 g) was mixed with 10% KOH solution (40 ml) and heated on a water bath for one hour. An appreciable amount of solid remained in the solution throughout this time, and at the end it was filtered off from the hot solution, washed with water, and dried. The 4-piperonyl-2-imidazolidone was recrystallized from dilute alcohol (one part of alcohol and three parts of water); the melting point was 207°. When the alkaline solution was cooled, a further crop of 4-piperonyl-2-imidazolidone was obtained: the total yield was 1.24 g (93.2%). Acidification of the alkaline solution yielded benzoic acid (0.7 g).

	Found %: C 58.16; 58.20;	H 6.92; 6.90;	N 13.60; 13.64
$C_{16}H_{10}O_3N_2$.	Calculated %: C 58.24;	H 6.84;	N 13.58

SUMMARY

1. A general method has been developed for the preparation in good yield on N-benzoylated imidazolidone derivatives by the Curtius reaction, which is applied to esters of N-benzoylated β-amino acids.

2. The reaction has been carried out with N-benzoyl-β-phenyl-β-alanine, N-benzoyl-β-(m-nitrophenyl)-β-alanine, and N-benzoyl-β-piperonyl-β-alanine.

3. It has been found that reaction of excess of hydrazine hydrate with N-benzoyl-β-(m-nitrophenyl)-β-alanine yields the hydrazide of β-(m-aminophenyl)-N-benzoyl-β-alanine, i.e., reaction is accompanied by reduction of the nitro group.

LITERATURE CITED

[1] V.M. Rodionov and V.K. Zvorykina, Bull. Acad. Sci., U.S.S.R., Div. Chem. Sci., 3, 216, (1943).

[2] M N. Meisel, Biochem., 14, 361 (1949).

[3] V. M. Rodionov and V. V. Kiseleva, J. Gen. Chem. 18, 1906 (1948); V. M. Rodionov and B. I. Kurtev, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 1, 113 (1952)*; ibid., 2, (1952)**; V. M. Rodionov and T. S. Kiseleva, Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci., No. 2, 278 (1952)***

[4] V. M. Rodionov and N. N. Bezinger, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 4, 696 (1952).****

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* See Consultants Bureau translation, p. 123.
** " " " , p. 285.
*** " " " , p. 293.
**** " " " , p. 637.

ORGANOMETALLIC "BIURET" PROTEIN COMPLEXES

K. T. Poroshin

Work on organometallic "biruet" protein complexes is acquiring ever increasing significance for the study of protein structure. Recent work of Soviet investigators [1] on the study of the copper complexes of amides and amino acids and of the organometallic "biuret" complexes of amidines and peptides has enabled the characteristic properties of these complexes to be determined and has led also to conclusions concerning their structure. Studies of "biuret" protein complexes have been made by Gavrilov, Paradashvili, and Govorov [2], by Jesserer [3], by Plekhan [4], and by others, but these investigations have suffered from a serious defect, in that casual protein preparations, not characterized by any chemical or physicochemical methods, have been taken for investigation.

The present work is concerned with spectrophotometric investigation of copper "biuret" complexes of certain proteins. The protein preparations investigated were: casein prepared according to Hammarsten, glycinin (soya bean protein), legumin (protein from peas), and gelatin. Also, we made special protein preparations, namely, so-called "proto-acids", which were isolated from vegetable and animal materials by the well known method due to Perov [5]. We investigated casein and fibrin acids and also preparations isolated from peas, oats and grain.

The characteristics of protein preparations obtained in the form of proto-acids are given in Table 1.

TABLE 1

Chemical and Physicochemical Characteristics of Protein Preparations

Characteristic		Protein preparation			
		casein	fibrin	oats	peas
Titration No.		8.35	9.3	8.09	9.10
Refractive index		1.3350	1.3348	1.3350	1.3346
Viscosity		1.30	1.53	1.40	1.71
Surface tension		0.80	0.90	0.78	0.85
Conductivity, K x 10^5		48.25	47.07	55.00	58.48
Specific rotation		−95°	−85°	−82°	−91.50°
Amine N	(% on wt. of protein)	0.32	0.37	0.42	0.35
Total N		15.60	15.20	15.71	15.60
Amide N		1.62	1.75	1.80	1.90
Basic N		3.19	3.45	3.60	3.50
Monoamino-acid N		10.25	10.79	10.22	9.85

Note: A 1% solution of the protein in caustic soda was used for the physicochemical measurements. The equivalent amount of alkali, i.e., the amount necessary to convert the protein completely into proteinate, was taken: the amount required was calculated from the titration number. In the specific-rotation determination, a 1% solution of protein in 0.1 N alkali was used. The measurements were carried out at 18°.

The solutions of copper "biuret" complexes were prepared as follows. Caustic soda as a 3% solution (100 ml) was added to a 200-mg sample of the protein preparation. When the protein had dissolved, 0.25 M copper acetate was added to the alkaline solution in small portions at a time until permanent flocs of copper hydroxide remained. After one hour the precipitate of copper hydroxide, was centrifuged off, and the colored solution of the copper "biuret" complex was subjected to spectrophotometric investigation. Spectrophotometric curves were obtained with the aid of a Konig-Martens spectrophotometer. Results of spectrophotometric determinations on solutions of copper "biuret" complexes of Hammarsten casein, glycinin, legumin, and gelatine are given in Table 2.

Spectrophotomeric absorption curves for solutions of copper "biuret" complexes of these proteins are shown in Figure 1.

As will be seen from the figures given in Table 2 and from the absorption curves (Fig. 1), all of these proteins, with the exception of gelatin, have a single absorption maximum at 560 mμ. The maximum for gelatin is displaced towards the longer waves (570 mμ). The variation in intensity of absorption is characteristic of these preparations and points to a variation in the structure of the copper "biuret" complex for the separate components of the

TABLE 2

Values of ϵ* for Solutions of Copper "Biuret" Protein Complexes

Wavelength (mμ)	Hammarsten casein	Glycinin	Legumin	Gelatin
480	0.1120	0.2275	0.2130	0.2512
505	0.2315	0.2750	0.2520	0.3620
530	0.3250	0.3470	0.2980	0.4553
550	0.3760	0.3830	0.3310	0.5020
560	0.3880	0.3935	0.3487	0.5120
570	0.3712	0.3765	0.3312	0.5329
580	0.3507	0.3620	0.2768	0.5005
610	0.3015	0.3245	0.2315	0.4112
630	0.2610	0.2753	0.2248	0.3528
690	0.1468	0.1674	0.0870	0.0201
730	0.0685	0.0735	0.0129	0.0120

* ϵ is a measure of light absorption

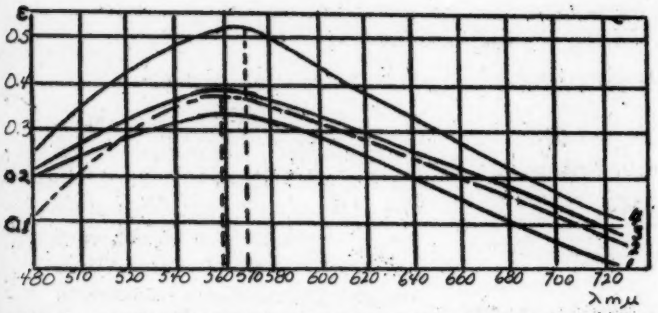

Fig. 1. Spectrophotometric absorption curves for solutions of copper "biuret" complexes of proteins. 1) Legumin; 2) Hammarsten casein; 3) glycinin; 4) gelatin.

TABLE 3

Amount of Copper Bound in "Biuret" Protein Complexes

Protein	Amount of protein (g)	Amount of copper required for formation of:				
		Complex with whole of protein (mg)	"Red" complex		"violet" tripeptide complex	
			in mg	in %	in mg	in %
Gelatin.	1.25	140.0	8.4	6.0	131.6	94.0
Legumin	1.32	187.1	9.91	5.3	177.19	94.7
Glycinin	1.35	236.5	10.1	4.24	226.4	95.75
Hammarsten casein	1.17	134.5	9.81	7.3	124.69	92.70

The absorption curves for solutions of copper "biuret" complexes of proteins of the proto-acid type are given in Figure 2.

protein macromolecule that form so-called "red biuret complexes" with copper. In order to confirm this, the relative amounts of copper required for formation of the "red" and of the "violet" complexes were determined by the method of differential spectrophotometry that we have developed [6]. The results of the investigation are given in Table 3.

From analysis of the data in Table 3 we may conclude that the protein preparations investigated – Hammarsten casein, gelatin, and also vegetable proteins, isolated by the so-called, classical, salt method – differ from one another both in the total amount of copper required for "biuret" complex formation with the protein, and also in the relative amounts of copper required for formation of "red" (tetra-, penta-, and hexa-peptide) and "violet" (tripeptides) complexes. The amount of copper required for formation of the "red" complex is greatest for casein (7.3%); gelatin comes next (6.0%), and the vegetable proteins have still lower values: 5.3% for legumin and 4.24% for glycinin. The greater part of the protein is made up of components that give "biuret" complexes of a tripeptide character with copper, the relevant figures being: casein 92.7%, legumin 94.7%, glycinin 95.76%, and gelatin 94.0%.

The spectrophotometric investigation of these proteins was followed by a similar investigation of protein preparations isolated as "proto-acids". Solutions of their copper "biuret" complexes were prepared as for the other protein preparations. The results of spectrophotometric studies of the complexes of proteins isolated according to the method used for the preparation of casein proto-acid are given in Table 4.

TABLE 4

ε-Values for Solutions of "Biuret" complexes of Proteins Isolated by the Method Used for the Preparation of Casein Proto-acid

Wavelength (mμ)	Casein	Fibrin	Pea protein	Oat-grain protein
480	0.1735	0.1552	0.1950	0.1743
505	0.2538	0.2458	0.2672	0.2457
530	0.3418	0.3310	0.3575	0.3179
550	0.4025	0.3920	0.4182	0.3743
560	0.4269	0.4115	0.4388	0.4076
570	0.4035	0.3840	0.4250	0.3790
580	0.3958	0.5720	0.4062	0.3693
610	0.3140	0.3012	0.3328	0.3005
630	0.2745	0.2507	0.2817	0.2537
690	0.1250	0.1138	0.1513	0.1230
730	0.0462	0.0430	0.0527	0.0537

From analysis of the experimental data in Table 4 and the curves in Figure 2 we may conclude that solutions of copper "biuret" complexes of protein preparations of the proto-acid type have absorption maxima at 560 mμ. The intensity of absorption is practically the same for all of the protein preparations, the greatest difference being observed at 580 mμ between pea and oats protein; the difference attains the value 0.0359. In proteins isolated by other methods, not only is there a variation in absorption maximum (gelatin 570 mμ, Hammarsten casein 560 mμ), but also a considerable variation in intensity of absorption. For example, the maximum difference in light absorption between gelatin and legumin copper "biuret" complexes at 570 mμ is 0.2007, i.e., almost ten times as great as for proteins of the proto-acid type. The curves for the proto-acids and for the so-called classical proteins are different in character.

By means of differential spectrophotometry on solutions of copper "biuret" complexes of proteins of the proto-acid type, estimations were made of the amount of copper required to form "biuret" complexes with the whole of the protein taken and also of the amounts required for formation of the red and violet components. The results are given in Table 5.

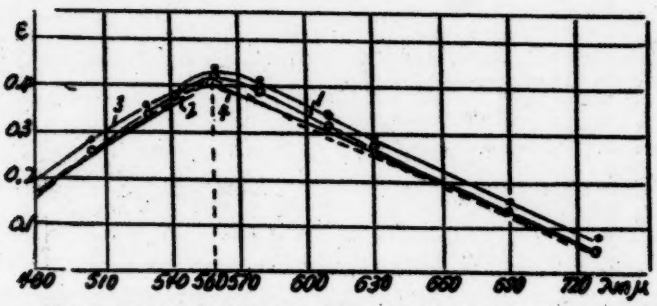

Fig. 2. Spectrophotometric absorption curves for solutions of copper "biuret" complexes of protein proto-acids: 1) casein acid; 2) fibrin acid; 3) pea protein; 4) oats protein.

TABLE 5

Amount of Copper entering into "Biuret"-Complex Formation in Proteins Isolated as Proto-acids

Protein	Amount of protein (g)	Amount of copper required for formation of: Complex with whole of protein (mg)	"Red" complex		"violet" tripeptide complex	
			in mg	in %	in mg	in %
Casein acid	1.15	130.8	9.2	7.03	121.6	92.97
Oats protein	1.20	137.5	9.55	6.95	127.95	93.05
Pea protein	1.10	131.0	8.9	6.79	122.10	93.21

The results in Table 5 indicate that peptide chains containing more than three amino-acid residues comprise 6.79-7.03% of the preparation for proteins of the proto-acid type. In proteins isolated by other methods (see Table 3), the corresponding figures vary from 4.25% (glycinin) to 7.3% (Hammarsten casein). As in the case of classical proteins, the amount present as peptide chains (trimers) in the proto-acids forms the main bulk of the protein macromolecule. In proteins of the proto-acid type, the amount of copper required for formation of the violet complex comprises 92.97-93.21% of the total amount of copper entering into "biuret" complex formation. For proteins obtained by other methods (Hammarsten casein, legumin, glycinin, gelatin), the methods (Hammarsten casein, legumin, glycinin, gelatin), the corresponding amount of copper varies over a wider range, namely, 92.70%-95.75%. These figures show that the protein proto-acids comprise more homogeneous fractions than proteins prepared by other methods do.

The spectrophotometric observations on solutions of organometallic "biuret" complexes of proteins of vegetable and animal origin show that they have absorption maxima at 560 mμ. If the protein macromolecule were in

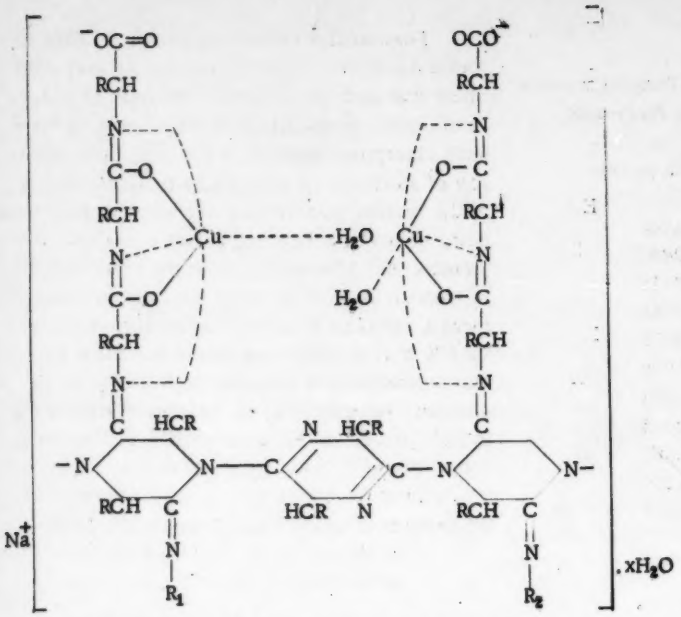

Fig. 3. Copper "biuret" protein complex, Structure 1.

the form of long polypeptide (polyamide) chains, as Fischer and Abderhalden supposed, the absorption maximum should be found at 505-520 mμ. If we accept the protein structure proposed by Zelinsky and Gavrilov [7], the structure of copper "biuret" complexes for fragments of protein microstructure may be represented as in Figures 3 and 4. We consider that the existence in the protein macromolecule of Structures 1 and 2 is confirmed by the present observations, as well as by other facts.

SUMMARY

1. Absorption-spectra curves have been obtained for solutions of the copper "biuret" complexes of vegetable and animal proteins isolated by various methods.

2. It has been shown that protein proto-acids comprise more homogeneous fractions than protein preparations obtained by other methods.

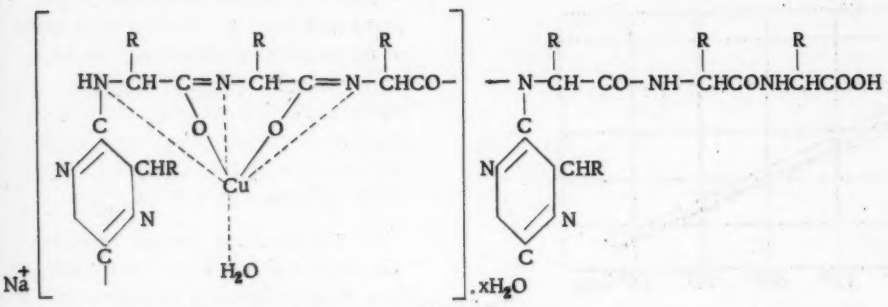

Fig. 4. Copper "biuret" protein complex, Structure 2.

3. A possible structure for the copper "biuret" complex of a microstructural protein fragment has been suggested.

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LITERATURE CITED

[1] N.I.Gavrilov, M.I.Plekhan, and N.A.Poddubnaya. Bull.Acad.Sci.USSR, Div.Chem.Sci., 127 (1941); N.A. Poddubnaya and N.I.Gavrilov. J.Gen.Chem., 18, 1848,1860 (1948); M.I.Plekhan and N.I.Gavrilov. J.Gen.Chem., 18, 1843 (1948); K.T.Poroshin. Sci.Communications of Members of D.I.Mendeleev All-Union Chem.Soc., 2, 3 (1949); M.I.Plekhan. J.Gen.Chem., 21, 312, 316, 574, 579 (1951)*; Chemistry and Physical Chemistry of Macromolecular Compounds, USSR Acad.Sci.Press, Moscow (1952) 116.

[2] N.I.Gavrilov, A.A.Paradashvili, and A.I.Govorov. Biochem., 4, 35 (1939).

[3] H.Jesserer. Biochem. Ztg., 285, 36; 287; 71 (1936).

[4] M.I.Plekhan. J.Appl.Chem., 13, 620 (1940).

[5] S.S.Perov. Biochemistry of Proteins, Sov.Sci.Press (1951).

[6] K.T.Poroshin. Collected papers: Investigations on Macromolecular Compounds, USSR Acad.Sci.Press (1949), p. 193.

[7] N.D.Zelinsky and N.I.Gavrilov. Bull. Moscow State Univ., 7, 57, (1947).

* See Consultants Bureau translation, p. 341, 347, 635, 641

CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

COMMUNICATION 8. HYDROCONDENSATION OF CARBON MONOXIDE WITH 2-METHYLPROPENE

Ya. T. Eidus, K. V. Puzitsky, and M. I. Batuev

The reaction of catalytic hydrocondensation of carbon monoxide with olefins has now been carried out with ethylene [1-5], propene [6,7], and butene [7,8]. It was of interest to extend this reaction also to olefins having a branched carbon chain, and the present work had as its object the investigation of the hydrocondensation of carbon monoxide with a 2-methylpropene-hydrogen mixture, 2-methylpropene being taken because it is the simplest branched olefin. The apparatus and procedure were the same as in the previous investigations [2].

The 2-methylpropene used in the preparation of the initial gas mixture was obtained by dehydration over aluminum oxide of isobutyl alcohol having the following constants: b.p. 107-107.5°, d_4^{20} 0.8040; n_D^{20} 1.3954. The 2-methylpropene that was collected was fractionated, and the fraction of b.p. −6° was taken; it was completely absorbed by 63% sulfuric acid.

EXPERIMENTAL

In Table 1 results are given of experiments on an equimolecular mixture of 2-methylpropene and hydrogen containing 5-6% of carbon monoxide; the reaction was carried out at 190° and atmospheric pressure over two specially prepared catalysts, No. 42 and 43 (30 cc of each). The starting mixture had the following average composition: 45-50% 2-methylpropene, 40-45% hydrogen, and 5-6% carbon monoxide.

TABLE 1

Catalyst No.	Expt. No.	Duration of expt. (hr)	Space velocity (liter/liter.hr)	Concentration (%)	Mean yield (ml/cu. m)				Mean yield, L + H, (ml/liter.hr)	Maximum yield, L + H	
					heavy oil (H)	light oil (L)	L + H	water		(ml/cu.m)	(ml/liter.hr)
42	203	29	122	54.0	361	254	615	38	69.3	731	83.2
42	204	24	121	53.3	346	252	598	38	67.5	784	86.6
42	205	24	124	55.0	345	304	649	35	74.7	696	82.0
42	206	24	123	53.0	295	255	550	45	62.0	780	86.3
43	207	12	101	54.1	273	214	487	36	45.6	653	61.2
43	208	48	101	45.6	291	259	550	39	51.0	633	58.4
43	209	24	104	52.2	246	294	540	49	52.2	644	63.8

As will be seen from Table 1, this mixture readily undergoes the hydrocondensation reaction with formation of a liquid condensate in considerable yield. Catalyst No. 42 was particularly active: at a space velocity for the original gas of 120, the yield of condensate was, on the average, 550-650 ml/cu.m of catalyst per hour (62-69 ml/liter of catalyst per hour), and the maximum yield in the individual six-hour experiments attained 785 ml/cu. m, or 87 ml/liter. hr. Catalyst No. 42 was working for 101 hours with three regenerations (every 24 hours), and the total amount of oil (light and heavy) obtained by its aid was 206 ml. The less active catalyst, No. 43, working at a space velocity of about 100, gave an average yield of 487-556 ml/cu.m, or 45-52 ml/liter. hr; it had a working period of 84 hours, being regenerated after Expt. 207 and Expt. 208, and the total amount of oil obtained by its aid was 125 ml. These results show that the reaction rate for 2-methylpropene is not less than that of butene on Catalysts No. 29-33 [7,8].

The condensates obtained using the two catalysts were mixed. The oil was separated from water formed in the reaction and was then washed, first with caustic soda solution, and then three times with water; part of it was dried over anhydrous sodium sulfate. The dry oil had the following constants: d_4^{20} 0.6866, n_D^{20} 1.3930, and bromine number 20 (11% unsaturated hydrocarbons). Debutanization experiments showed that it contained in the

dissolved condition about 5% by volume of "gas oil" (C_4).

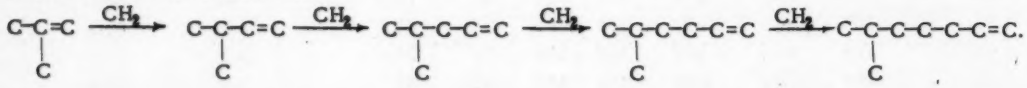
The other part of the oil (210 ml) was hydrogenated over Raney nickel (10-12%) in a half-liter autoclave at 200° at 120-130 atm for 10 hours. The hydrogenation product was filtered from the nickel and dried over anhydrous sodium sulfate; it had the following constants; d_4^{20} 0.6909; n_D^{20} 1.3964; and bromine number 2.

TABLE 2

Fraction No.	Boiling range (°C)	Vol.% of orig. oil	d_4^{20}	n_D^{20}	C_x	Hydrocarbon
1	21-28	2.7	0.6158	–	C_5	(Isopentane)
2	28-28.5	7.1	0.6196	1.3535	C_5	Isopentane
3	35-36	1.8	0.6246	1.3567	C_5	Pentane
4	49-58	0.9	0.6378	1.3648	C_6	
5	58-59	1.8	0.6502	1.3705	C_6	2-Methylpentane, 2,3-dimethylbutane (?)
6	60	14.3	0.6527	1.3710	C_6	2-Methylpentane
7	61-67	5.4	0.6603	1.3747	C_6	
8	68-89	4.0	0.6799	1.3851	C_7	
9	90-91	13.8	0.6836	1.3867	C_7	Mixture of 2-methylhexane and 3-methylhexane
10	92-113	8.0	0.6969	1.3930	$C_7 + C_8$	
11	114-118	8.0	0.7029	1.3967	C_8	2-Methylheptane
12	118-140	7.2	0.7151	1.4029	$C_8 + C_9$	
13	141-157	11.6	0.7258	1.4087	$C_9 + C_{10}$	
14	160-210	8.9	0.7473	1.4187		
15	210-291	4.5	0.7498	1.4281		
Original oil	21-291	–	0.6909	1.3964		

A part of the hydrogenated product (115 ml) was fractionated through a column of 40 theoretical plates. There was about 3 ml of gas oil, and the remaining 112 ml was separated into 13 fractions over the range 21-157° and residue; 86.6% came over below 157° (762 mm). The residue (13.3%) was distilled from a Favorsky flask. All of the fractions obtained are given with their properties in Table 2. The curve for the fractionation through the column is given in the accompanying diagram.

As will be seen from Table 2 and from the diagram, the fractions obtained in high yield correspond mainly to products formed by the lengthening of the main chain. Actually, Fraction 2 (28-28.5°; 7.1%) corresponds to 2-methylbutane, Fraction 6 (60°; 14.3%) corresponds to 2-methylpentane, Fraction 9 (90-91°; 13.8%) corresponds to 2-methylhexane, and Fraction 11 (114-118°; 8.0%) corresponds to 2-methylheptane. These results show that reaction proceeds by stepwise lengthening of a straight chain, in steps of one carbon atom:

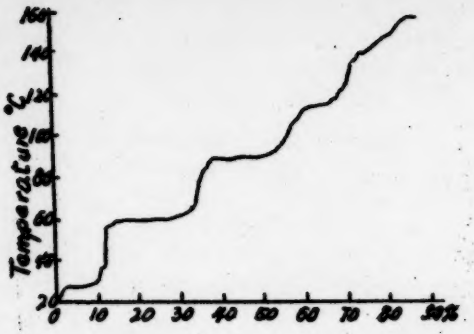


The contents of the C_5-, C_6-, C_7-, and C_8-fractions in the condensate were approximately 12,22,22 and 12% respectively.

The results of the fractionation were verified by the Raman-spectrum method. It was found that Fraction 6 consisted almost entirely of 2-methylpentane, which was estimated by reference to the following frequencies: 325 (9.5, 387 (2,b, double), 446 (15), 734 (3.8), 785 (2), 815 (28), 860 (2), 894 (5.7), 942 (3,b), 958 (9), 1015 (2), and others. Fraction 9 consisted practically entirely of 2-methylhexane, which was determined by reference to the following frequencies: 308 (13), 414 (3.5), 434 (4.5), 448 (1), 729 (2), 784 (5.4), 823 (11.2; sh), 874 (6.4), 894 (9.5, sh), 940 (3), 956 (6.3), 1062 (5.6, b), and others. Fraction 12 consisted mainly of 2-methylheptane, detected by the following frequencies: 288 (11.1), 409 (3.5), 763 (2.6), 816 (9.2), 879 (2.7), 895 (4.5), 952 (5.6; sh), 963 (5.6;sh), 1030 (2), 1044 (3) and others. Fraction 10 contained 2-methylhexane and 2-methylheptane, the former predominating; they were detected by the same frequencies as those cited above for Fractions 9 and 12.

SUMMARY

1. The reaction of catalytic hydrocondensation of carbon monoxide with straight-chain olefins has been extended to the simplest branched olefin, 2-methylpropene.



2. The average yield of liquid condensate was 550-650 ml/cu.m, or 62-69 ml/liter.hr, and the maximum yield attained 785 ml/cu.m, or 87 ml/liter.hr.

3. The liquid condensate contained 11% of unsaturated hydrocarbons and, after complete hydrogenation, 86.6% distilled over below 157°. The contents of C_5-, C_6-, C_7-, and C_8- fractions were 12, 22, 22 and 12% respectively. These fractions consist essentially of hydrocarbons having a methyl side group on the second carbon of the chain, i.e. 2-methylbutane, 2-methylpentane, 2-methylhexane, and 2-methylheptane respectively.

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LITERATURE CITED

[1] Ya. T. Eidus and K. V. Puzitsky, Proc. Acad. Sci. USSR 54,35 (1946).

[2] Ya. T. Eidus, N. D. Zelinsky, and K. V. Puzitsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 1, 110 (1949).

[3] Ya. T. Eidus, N. D. Zelinsky, and K. V. Puzitsky, ibid, No. 3, 326 (1949).

[4] Ya. T. Eidus, N. D. Zelinsky, and N. I. Ershov, Proc. Acad. Sci. USSR, 60, 599 (1948).

[5] Ya. T. Eidus, N. D. Zelinsky, N. I. Ershov, and M. I. Batuev, Bull. Acad. Sci. USSR, Div. Chem. Sci. No. 4, 377 (1950).

[6] N. D. Zelinsky, Ya. T. Eidus, K. V. Puzitsky, and M. I. Batuev, Ibid. No. 6, 647 (1950).

[7] Ya. T. Eidus, N. D. Zelinsky, K. V. Puzitsky, and N. I. Ershov, ibid, No. 1, 145 (1952).*

[8] Ya. T. Eidus, N. I. Ershov, M. I. Batuev, and N. D. Zelinsky, ibid, No. 6, 722 (1951).

* See Consultants Bureau translation, p. 157.

C H R O N I C L E

CONFERENCE ON THE TRANS-EFFECT PRINCIPLE

On 24-26th of March, 1952, a conference was held in Moscow on the trans-effect principle. It was organized by the N. S. Kurnakov Institute of General and Inorganic Chemistry of the USSR Academy of Sciences, and leading academic and industrial specialists on the chemistry of complex compounds, from Moscow, Leningrad, Kiev, Ivanov, Tbilisi, Kazan, Kishenev, Dnepropetrovsk, and other towns, took part in the proceedings. The problem put before the conference was that of finding methods of approach and experimental techniques that could lead to the establishment of the nature and quantitative characteristics of the trans-effect principle. The qualitative side of this principle and its importance in science and industry are now well understood: it is widely applied in the synthesis of new compounds and is of great significance for the further development of chemistry and modern technology; it is a concrete application of Butlerov's theory of chemical structure to the complex-compound field.

The discussion was opened by Academician M. M. Dubinin, secretary of the Division of Chemical Sciences of the USSR Academy of Sciences. "The present conference," he said, "being devoted to the discussion of one of the fundamental questions in the theory of the structure of inorganic complex compounds, is closely concerned with concepts based on a more general principle, discovered by Butlerov, and developed by Markovnikov and others. We may therefore regard the work before us as a further stage in the creative development by Soviet scientists of the theory of chemical structure. On the basis of numerous experimental investigations, commenced already during the lifetime of L. A. Chugaev, I. I. Chernyaev succeeded in establishing that mutual effects, precisely analogous to those found in organic chemistry, occur between atoms in the inner zone of complex compounds. The basic idea of the Chernyaev generalization, which is known as the trans-effect principle, is as follows: the strength of the bond between the central metal atom and any substituent is affected very little by the nature of adjacent atoms or groups of atoms, whereas atoms or molecules situated in a more remote region of the inner zone of the complex compound —that is to say, in the trans position—have a powerful effect on the chemical mobility and reactivity of this atom of the complex compound.

"During the 25 years that have elapsed since the discovery of the trans-effect principle it has received a sound experimental basis both in the investigations of Academician I. I. Chernyaev and his students, and also in those of other workers on the chemistry of the platinum metals. The range of the applicability of the principle has been greatly widened in recent years, and, as a result, Soviet chemists have been enabled to direct the course of chemical processes relating to complex compounds and to make a rational approach to the synthesis of compounds of previously determined composition and structure.

"Nevertheless, the physical nature of the trans effect still has no adequate theoretical basis. Investigations on the quantitative characteristics of the trans effect are still in the initial stages: their development is doubtless hindered by the greatly inadequate amount of material available on the application of the great variety of physical and physicochemical methods of investigating complex compounds. Another important direction of research comprises the development of L. A. Chugaev's views on the widening of the concept of the complex compound and the extension of this concept and its associated laws to derivatives of as many elements as possible. This path will lead to the removal of the chemistry of complex compounds from an isolated, circumscribed section of chemistry, essentially concerned with compounds of the so-called noble metals. Other important questions of principle are involved in the development of the theory of the structure of complex compounds: the causes underlying the trans effect may be similar to or identical with the causes underlying the mutual effects of atoms in the molecules of organic substances.

"Free discussion on all these questions, under the conditions for the development of true bolshevist criticism and selfcriticism, will enable us not only to appreciate the fundamental objective results of the theoretical and experimental investigations into the chemistry of complex compounds, but also to plan our further course of progress in conjunction with the development of our advancing materialistic theory of chemical structure".

The conference heard and discussed two papers: "The Experimental Basis of the Trans-effect Principle" by Academician I. L. Chernyaev, and "The Explanation of the Trans Effect" by Corr. Member A. A. Grinberg.

In Academician Chernyaev's paper on the experimental basis of the trans-effect principle the results of the lecturer and his school (A. D. Gelman, V. I. Goremykin, A. M. Rubinshtein, A. V. Adrianova, L. A. Nazarova, and others) were cited in confirmation of the fruitfulness and progressive role of the trans-effect principle, which is based on the further development of the materialistic structural theory of Butlerov and Markovnikov in its application to inorganic complex compounds. The trans-effect principle may be formulated as follows: in complex molecules having the form of a square or octahedron in the center of which the central metal atom is to be found, the reaction rate for the substitution of an addend (in the form of an atom or molecule) bound to the central atom is determined by the nature of the substituent-addend occupying the opposite end of the diagonal. Thus, the strength of the bond between the central atom and any substituent is affected to a very small extent by the nature of adjacent (cis) atoms or molecules, whereas atoms or molecules situated in the most remote part of the complex-compound molecule (trans) on the diagonal of the square or the axis of the octahedron greatly influence the chemical behavior of the complex molecule.

The value of the trans-effect principle as a scientific generalization lies also in the fact that it has not only explained the courses of reactions in the inner zone of complex compounds and not only unified and explained the previously discovered rules of Jorgensen, of Peyronel, and of Kurnakov, but has also brought them together to form a single, orderly whole and made it possible to predict the course of inner-zone reactions, even though the nature and quantitative side of this principle still remains unelucidated.

In Corr. Member Grinberg's paper a description was given of the attempts that have been made at various times by Soviet workers to explain the trans-effect principle; they are briefly as follows: Grinberg, and then Nekrasov, tried for the first time to make an approach to the elucidation of the nature and quantitative characteristics of the trans-effect principle starting from polarization concepts. Grinberg argued, that if in a complex compound having the form of a square three identical acid residues (addends) of identical polarizability are placed at corners and an acid residue (addend) differing from the other three and having a high polarizability is placed at the remaining corner, then, owing to the displacement of the center of gravity of negative charges in the direction of the substituent in the trans position to the fourth acid residue, the acid group at the opposite end of the diagonal to the fourth acid residue is weakened. Corr. Member B. V. Nekrasov in his solution of this problem started from the idea of a dipole induced in the central ion. When the acid residues (addends) are identical, an identical dipole is induced in each by the positive central complex-forming ion, leading to a strengthening, to an equal extent, in each of these bonds with the central ion. If one of the acid residues is replaced by another, different residue, a resultant dipole arises in the complex-former which depends on the nature of the newly introduced acid residue, and this is the greater in value, the greater the difference between its polarization properties and those of the other three groups. In other words, the deformability of the complex-former depends on whether the acid residue (addend) last introduced into the molecule of the complex compound has a greater or less polarizability. Thus, according to Grinberg and Nekrasov, the trans effect "is a special case of the phenomenon of contrapolarization".

The conference found that both of these treatments permitted limited, tentative, qualitative approaches to the elucidation of the nature and quantitative aspects of the trans-effect principle. The concepts developed by Grinberg and Nekrasov have now lost much of their value and may be regarded only in their historical perspective. It must be noted that these so-called polarization concepts are based on methodological errors, for they are based largely not on facts, not on direct experimental data, but on a great number of assumptions in calculations that do not really reflect any real phenomenon and cannot, therefore, characterize the nature and quantitative aspects of the trans effect. There have been also other attempts to elucidate the physical aspects of this principle, based on the establishment of the nature of the chemical bond between the central atom and a substitutent (Chernyaev and Gelman) and on the oxidation-reduction properties of inner-zone substituents (Grinberg). At the conference, also other ways of achieving this end were discussed; they were based on various principles, but they permitted the solution of the problems that had been set — the elucidation of the nature and quantitative characteristics of the trans-effect principle.

The papers of Academician Chernyaev and Corr. Member Grinberg contained certain errors of historical, scientific, and methodological character. In these papers there was to be found either none or very little reflection of the work of prominent Russian chemists such as Lomonosov, Mendeleev, Kurnakov, and Chugaev. In these papers no use was made of many of the investigations of Soviet scientists. In Corr. Member Grinberg's paper

there was no clear formulation of the speaker's attitude to the so-called "theory" of resonance-mesomerism, which has so deleteriously affected progress in the chemistry of complex compounds. Hence, both of these speakers were justifiably criticized.

The papers gave rise to many questions and to a lively discussion, in which specialists in various branches of knowledge — chemists, physical chemists, and physicists — took part. The participants characterized in detail the prominent role and great significance of the trans-effect principle in the chemistry of complex compounds. Attention was drawn to the inadequate use that was being made of modern physicochemical and physical methods in the work directed to the elucidation of the trans-effect principle.

Professors Kedrov, Goremykin, and Gelman, in their speeches, discussed in detail the genealogical link connecting Chernyaev's trans-effect theory with the principles of Butlerov's materialistic theory of chemical structure, and they emphasized the great harm done by the anti-Butlerov, antiscientific, basicly idealistic concept of resonance-mesomerism, both in organic, and in inorganic chemistry.

Participants of the conference, particularly Professors Boky, Yakshin, Yatsimirsky, Babaev, and Ptitsyn, stated and considered the unanswered and disputed questions concerning the fundamental nature of the trans effect and the methods of solving this problem. They considered that polarization concepts based on electrostatics could not be of any help in the elucidation of the complex nature of the trans-effect principle. As is known, the attempts of Corr. Member Ya. K. Syrkin, on the basis of the erroneous concept of resonance-mesomerism, to replace the trans effect by cis-reinforcement did not in fact lead him to a positive solution of this problem, but had, on the contrary, a harmful effect and delayed for some time the normal development of this remarkable principle.

The participants of the conference unanimously condemned the so-called theory of resonance-mesomerism, which is fundamentally idealistic, as being pseudoscientific, and they brought forward a number of concrete proposals concerning the planning and coordination of scientific investigations in this branch of inorganic chemistry. Reference will now be made to the speeches of some of the participants of the conference on the trans-effect principle.

Prof. A. V. Babaeva paid a high tribute to the trans-effect principle, and she cited as an example of its value the fact that no platinum complex compound of the cis-diamine series containing hydroxylamine had been prepared in 70 years; now, guided by the trans-effect principle of Chernyaev, she had succeeded in bringing about this synthesis.

Prof. K. B. Yatsimirsky remarked that Grinberg in his paper had expressed pessimism in connection with the fact that no complete theory of the trans effect exists as yet. This is not altogether correct, the speaker pointed out. We must ask ourselves the question: What is a theory? If we answer that a theory is a generalization from experiment, then in this case we have a wide generalization from experiment, so that there is indeed already a theory. With regard to its interpretation, the matter is certainly not hopeless, as it might appear at a first glance. Yatsimirsky remarked that to limit the trans-effect principle only to kinetics would be harmful, because in fact we have to deal with two groups of complex compounds, which are different in principle: those which react in time, and those for which kinetics does not exist, i.e., those complex compounds that are broken down and formed instantaneously.

Prof. V. I. Goremykin said that, if we compare the results obtained by the Chugaev-Chernyaev school with the work done in this field abroad, it is easy to see that the work of the scientists of capitalist countries is distinguished by the absence of any such unifying idea; it may be characterized briefly as a jumble of ideas or as pure, undisguised empiricism. The leading role of the Chugaev-Chernyaev school of inorganic chemists, both in the USSR and elsewhere, can therefore be understood. Goremykin pointed out further the necessity of developing further the trans-effect principle, giving first consideration to the synthesis and investigation of the complex compounds of different metals, carrying out syntheses both in aqueous, and in nonaqueous solution, and studying the properties of complex compounds by modern physicochemical and physical methods. The speaker then pointed out the erroneous statement contained in the foreword to Chernyaev's and Grinberg's papers. It is there stated: "Investigation by the aid of X-radiograms can in principle replace the determination of molecular structure by chemical means". This statement is erroneous from the methodological point of view, for X-ray-structure analysis cannot replace all the variety and richness of chemical investigation.

Prof. G. B. Boky remarked that neither in the papers that had been given, nor in the introductory statement of the organizing committee were there any references, apart from some vague allusions, to the discussion "The

State of the Theory of Chemical Structure in Organic Chemistry". "It is well known," said Boky, "that the trans-effect principle was discovered and developed in the Soviet Union, and that practically no-one has denied the existence of the trans effect, the exceptions being a statement made long ago by Corr. Member I. A. Kazarnovsky in which he threw doubt on the priority of the discovery and its importance, and an unsuccessful attempt by Corr. Member Syrkin to show "theoretically" that the trans effect is only an apparent effect that is bound up with the concept of "cis-reinforcement". Neither of these assertions have received wide acceptance and have not had any essential effect on the development of work on the trans effect. Concerning the trans effect, we may now speak only of its being undervalued, of its being ignored, but not of its being criticized. The ways of the further development of the theory of the trans effect have not been indicated clearly in the papers; and yet the indication of these ways and the intelligent planning of research over a long period of time forms are the objectives of our conference, and these matters are always of prime importance and are often subjects that are ripe for discussion.

An important defect in both papers, in the speaker's opinion, was the complete disregard of the results obtained in recent years in crystal chemistry, developed on the basis of the immortal work of E. S. Fedorov. Another defect in Chernyaev's paper was undoubtedly the extreme narrowness of treatment. All the examples, without exception, were taken from the chemistry of platinum, whereas one of our primary problems is the extension of the trans-effect principle to other substances and to other fields in chemistry. Boky then discussed the way in which crystal-chemical and X-ray-structure methods enable us to approach the structure of complexes in its quantitative aspects; they enable us to measure the lengths of the coordinates of the complexes in centimeters, i.e., to measure the interatomic distances. The methods of classical chemistry do not offer such possibilities, and the ignoring of such material in Chernyaev's paper is therefore particularly to be regretted, for it is difficult to imagine that these methods are not known to him. A fundamental defect of Grinberg's paper is the exaggeration of the significance of electrostatic concepts, and again we find undervaluation of crystal-chemical data. Our most important immediate task, in the speaker's opinion, is the extension of investigations relating to the direct determination of magnitudes that characterize the effect quantitatively.

Ya. A. Fialkov, Corr. member of the Ukr.SSR Academy of Sciences, spoke of certain questions that had been discussed in connection with the problem of the trans-effect principle. The definition of the trans-effect principle formulated by the Organizing Committee merits, according to Fialkov, great attention in that it is based on the sum total of all the experimental results relating to the trans-effect principle. It does not go outside the limits of experiment, and, moreover, it defines a number of directions in which the further coordinated studies of this important theoretical generalization must proceed. It is impossible to agree completely with the formulation of the definition of the concept of the trans effect as given in the Organizing Committee's preamble, for it is not in conformity with Butlerov and Markovnikov's concept concerning the mutual effects of atoms bound together in a molecule.

B. M. Kedrov, Corr. member of the Ac ademy of Pedagogic Sciences, remarked that the main problem of the conference was the thorough, detailed application of the fundamental ideas of the Butlerov theory to inorganic chemistry and, in particular, to one of its most important branches, the chemistry of complex compounds.

"Grinberg stated," Kedrov pointed out, "that he regarded Chernyaev's discovery not as a simple observation, as a simple group of unsystematic, ungeneralized facts, but as the discovery of a definite principle, or even law. This is quite true, but I would say that Grinberg abases the meaning of this law, putting it on the level of a fact and saying, in effect, these are concepts of the same order, whereas the concept of the trans effect is not only the discovery of a definite bond and relationship, but also an interesting interpretation; and again, not only interesting, but also as deeply and seriously applicable to the present phenomenon as an interpretation in organic chemistry, for here we have indeed an extension of the Butlerov principle to the field of inorganic chemistry".

It has been considered until now that Mendeleev made no pronouncement on the question of complex compounds, or, as he said, "molecular compounds"; there is very little about this matter in "The Principles of Chemistry". Apparently, Mendeleev did not concern himself with this question, either experimentally, or theoretically. Kedrov pointed out that in the second edition of Grinberg's "Chemistry of Complex Compounds" it is stated that Mendeleev did not carry out any experimental work with complex compounds." This is not true. In the Leningrad Museum there are about ten manuscripts and many laboratory notes relating to the study of complex compounds. This is particularly interesting, because the fundamental idea that lies at the basis of not only this problem, but also the whole of the chemistry of complex compounds, the idea of a central atom, owes its origin directly to Mendeleev.

"I consider that all this material is of great interest, particularly the article in which Mendeleev generalizes his views, criticizing the erroneous views of his contemporaries and attempting to develop correct ideas concerning platinum compounds, ideas that are extremely close to later concepts and are much closer to our ideas than were those of his contemporaries."

Prof. A. D. Gelman pointed out that Werner's coordination theory did not in anyway provide a scheme covering the behavior of chemical processes in the inner zone of complex compounds. This failing of the theory was remedied by Chernyaev's work, and if we make a comparison with organic chemistry, it must be said that Chernyaev has carried out the work that was done in the field of organic chemistry by Butlerov and Markovnikov. Gelman's investigations on unsaturated compounds — carbon monoxide, nitric oxide, and thioethers —, and also Grinberg's work on phosphines, have shown that these unsaturated molecules show a still higher trans effect than acid residues. It was at this point that the speaker proposed that the range of the trans-effect principle should be extended beyond that formulated by Chernyaev in 1926, i.e. that it should be considered that the place where reaction occurs in the inner zone of a complex compound is in the trans position to the active substituent, which may be not only an acid residue, but also a compound such as a thioether, nitric oxide, or carbon monoxide.

In Gelman's opinion, it is incorrect to try to explain the trans effect from a single point of view, as Grinberg and Nekrasov have tried to do — at first from the polarization point of view, and now from the point of view of reducing properties. We must make our approach while taking into account the properties of the substituents that can enter and form a complex molecule.

G. S. Zhdanov devoted his speech to the question of the trans effect in solid crystalline substances and to the prospects of crystal-chemical methods of investigating the trans effect. He pointed out the problem is extremely difficult and complex. In fact, exploratory investigations are essential. Sometimes it is impossible to come to a precise conclusion, particularly in gaseous media and in solutions. More reliable results can be obtained in the solid state, but, if we turn to crystals, we are faced with the necessity of making extremely exact measurements of interatomic distances. It is now clear that the trans effect has a value of the order of several angstroms. In this connection, the recently published work of Boky is of great interest: results of investigations on complex compounds are given, including bond lengths of ammonia - platinum — chlorine.

Prof. B. V. Ptitsyn remarked that the trans-effect principle discovered by Chernyaev has one excellent characteristic, which is common to all great generalizations, namely, that one gets use to it fairly quickly, and fairly soon the time comes when it appears strange how it was possible to manage previously without this principle. Chernyaev, in his paper, gave a detailed and full account of the experimental material that lies at the basis of the trans-effect principle, and he pointed out the facts that cannot be fitted into the principle.

The quantitative characteristics of the trans-effect principle may be arrived at from the change in valency in the process of complex formation, of which Chernyaev spoke in his paper when he pointed out that the trans effect cannot be characterized in terms of the usual valency; this was referred to also by M. M. Yakshin in his speech. Thus, by a comparison of potentials, it is possible to evaluate the degree of covalency of the bond and, ultimately, the value of the trans effect.

Prof. A. V. Ablov pointed out that the trans-effect principle discovered by Chernyaev for bivalent platinum compounds generalized the results of experiments on complex compounds and enabled us to predict the chemical behavior of these compounds and to map out the way to the synthesis of new compounds. This principle was extended by Chernyaev to cobalt compounds, and there also it was found to be true and to give fruitful results. The reduction of the trans-effect merely to a question of the definition of directed bonds, i.e. to the fact that bonds are directed, would not explain the difference in behavior between bi- and quadri-valent platinum on the one hand, and tervalent-cobalt on the other. It is of course necessary for the existence of the trans-effect that bonds should be definite, but only directed bonds are sufficiently characteristic for the appearance of the trans-effect.

Prof. L. M. Volshtein remarked that the trans-effect principle is a valuable guide to action in the work of chemists in the field of the complex compounds of bi- and quadri-valent platinum. As had been said, the trans-effect was exhibited by the other metals of the platinum group to a considerably smaller extent. For metals that do not belong to the platinum family the trans-effect is, practically speaking, absent or only barely apparent. It is obvious that these non-noble metals, as we may term them briefly, must take part in the mutual effects of atoms and groups of atoms. No one doubts this, but whether it is the trans-effect that is displayed, or the free

action of addends situated in the trans-position, and to what extent it is displayed — these questions are difficult to answer in advance, while there are so few data concerning the trans effect for non-noble metals.

Others that joined in the discussion were Academician A. I. Frumkin, Prof. A. M. Rubinshtein, V. G. Tronev, A. V. Nikolaev, K. A. Semenchenko, and A. M. Klochko. There were twenty speakers in all.

When concluding statements had been made by Academician Chernyaev and Corr. member Grinberg, the conference carried a concrete resolution concerning the development of scientific research work on the chemistry of complex compounds.

Resolution of the Conference on the Trans-Effect Principle

Comrade J. V. Stalin, in his great work "Marxism and Questions of Linguistics", has clearly pointed the way that Soviet scientists must take for the further development of Soviet science in all branches of knowledge. Guided by Comrade J. V. Stalin's precept that "no science can develop or flourish without conflict of opinions, without freedom of criticism", Soviet scientists have recently held a number of creative discussions on various scientific questions.

The Conference on the Structure of Organic Compounds held in 1951 exposed the "Theory of Resonance or Mesomerism" as methodologically unsound, idealistic, and unfruitful, and it pointed out the way of further development in Soviet chemistry on the basis of the only correct scientific method of gaining knowledge — dialectical materialism.

Characteristics peculiar to our native chemistry are: the depth and wideness of our investigations, the linking of theory and practice, and the further development and utilization of our rich heritage from the great Russian chemists Lomonosov, Mendeleev, and Butlerov. Our native chemistry was always materialistic, and this tradition has received its further development in Soviet chemistry.

The last fifty years has seen the work in our country of such outstanding inorganic chemists as N.S. Kurnakov, who created a new chemical method (physicochemical analysis) and was a prominent investigator in the chemistry of complex compounds, and L. A. Chugaev, who founded the largest existing school of chemists working in the field of complex compounds.

There were attempts in recent years on the part of Ya. K. Syrkin and M. E. Dyatkina to drag the anti-scientific, ideologically unsound concept of resonance into inorganic chemistry also, and these attempts did not receive a timely and adequate check from inorganic chemists.

The trans-effect principle, as it developed, met with differing responses from foreign and from Soviet chemists. The foreign chemists either ignored it, or ascribed its discovery to foreign chemists. Certain Soviet chemists, for example L. A. Kazarnovsky and B. F. Ormont, have disparaged the role and importance of the trans-effect principle in the chemistry of complex compounds.

The Conference points out that Soviet chemistry occupies the first place in the world with respect to the synthesis, study, and application of complex compounds.

The trans-effect principle, which was discovered in 1926 by I. I. Chernyaev, is a further step forward along the road of progress in Soviet chemistry and is a creative act consequent on the fruitful scientific activity of the Russian chemists of the preceding epoch.

Chernyaev's principle is a concrete expression of A. M. Butlerov's theory of chemical structure in the field of complex compounds. This principle opens up the road to the synthesis of compounds having previously determined compositions, structures, and properties. The importance of the trans-effect principle in practice is exceptionally high: by its aid, numerous complex compounds of the platinum metals have been synthesized, new analytical methods have been developed, and technical processes for the preparation of platinum metals from new raw materials have been worked out.

The Conference notes that work on the elucidation of the nature of the trans-effect has been carried out by I. I. Chernyaev, A. A. Grinberg, B. V. Nekrasov, and A. D. Gelman, all of whom have played a positive part in the clarification of certain aspects of the trans-effect. At the same time, the Conference finds that the work done on quantitative aspects of the trans-effect is still inadequate.

The Conference considers that it is essential to intensify work in this direction in order to obtain the data necessary for the creation of a general theory of the trans-effect.

Studies of the trans-effect have been confined hitherto mainly to complex compounds of the platinum metals. However, investigations into the mutual effects of coordinated groups in complex compounds of other elements are being carried out in various cities in our country (Kiev, Leningrad, Ivanovo, Tbilisi, Kishenev, Dnepropetrovsk, etc.), but they are still inadequate.

The further development of these investigations is hindered by the absence of adequate coordination of scientific investigations in this field.

The most important problems in the development of the theory of the structure of complex compounds on the basis of the trans-effect principle and of the achievements of modern science are the following:

1. Determination of the quantitative characteristics of the trans-effect by various methods, namely:

a) classical chemical methods, with consideration of the effect of the medium;
b) crystal-chemical methods;
c) physicochemical and physical methods: labeled atoms, thermochemical and thermographical, electrochemical (conductivity, potential changes, polarography, ion transfer, etc.), electrical (dipole moment and dielectric constant determinations), X-ray-structure analysis, magnetometry, etc.

2. Further development of work on the synthesis of complex compounds of various elements, on the physicochemical study of their chemical structures, on their reactivities, and on their application.

3. In order to coordinate and plan scientific investigations in the field of complex compounds, the Conference considers that it is essential to set up a committee of the Council of the N. S. Kurnakov Institute of General and Inorganic Chemistry of the USSR Academy of Sciences. In particular, this committee will be given the task of composing a plan for research work in 1953.

4. In order to develop the study of the trans-effect from all sides, it is essential to bring in workers representing allied branches of science.

5. The USSR Academy of Sciences is asked to publish the transactions of this conference in the Bulletin of the Platinum Sector. They are asked also to speed up the publishing of selected works of L. A. Chugaev.

6. It is considered essential that selected works of Russian workers on the chemistry of complex compounds should be published.

7. It is considered essential that the Sixth All-Union Conference on the Chemistry of Complex Compounds should be called for January 1953.

The Conference calls upon all workers on the chemistry of complex compounds to develop further the use of criticism and self-criticism in scientific work, to unmask any attempts to intrude hostile ideology into science, to strengthen the link of theory with practice, and to make every effort to complete the historic task set by Comrade Stalin: ". . . . not only to equal, but to surpass in the near future the achievements of science in foreign countries"*.

Session in Honor of the Bicentenary of the Foundation of the Science of Physical Chemistry by M. V. Lomonosov

On May 28th, 1952 there was held a joint session of the Division of Chemical Sciences, the L. Ya. Karpov Physicochemical Research Institute of the Order of the Red Banner of Labor, and the Chemistry Faculty of the M. V. Lomonosov Moscow State University of the Order of Lenin, and papers were read in honor of the bicentenary of the foundation of the science of physical chemistry by M. V. Lomonosov: "M. V. Lomonosov, Founder of Physical Chemistry" by Prof. S. V. Kaftanov, "The Work of M. V. Lomonosov on Atomistics, and its Significance for the Development of Chemistry" by Prof. N. A. Figurovsky, and "M. V. Lomonosov's Investigations on Solutions" by Prof. S. V. Gorbachev.

Academician M. M. Dubinin, opening the session, spoke of the services that M. V. Lomonosov had rendered and of his great love of his own people, to whom he devoted his strength and that which was most dear to him — his science.

S. V. Kaftanov emphasized in his paper that among the famous men that had risen in the great Russian nation and had contributed immense riches to the treasure house of world culture, M. V. Lomonosov occupies a special

place: his dissertation "The Action of Chemical Solvents in General" (1743) constituted the first work in physical chemistry. Of this paper Lomonosov himself wrote: "This theory of solutions based on chemical experiments and physical principles is the first example and pattern for the foundation of true physical chemistry. . .". Throughout his scientific career, Lomonosov was an advocate for the wide application of physics, chemistry, and mathematics in investigations. These sciences are found applied in combination in his crowning work: "Introduction to True Physical Chemistry" (1752).

In his paper N. A. Figurovsky referred to the definition of physical chemistry given 200 years ago by M. V. Lomonosov: "Physical chemistry is the science that explains on the basis of physical laws and experiments that which occurs in mixed chemical bodies subjected to chemical operations. It may be called chemical philosophy, but in a completely different sense from the mystical philosophy in which not only are no explanations given, but even the operations themselves are carried out in a mysterious manner. We decided to call this work physical chemistry because we had determined to include in it only that which would lead to a scientific explanation of the mixing of bodies. We therefore consider it essential to exclude everything relating to economic sciences, to pharmacy, to metallurgy, to glass technology, etc. and to place these subjects in a special course of technical chemistry." The speaker said also that physical chemistry has now penetrated into the whole of modern science and technology and that there was no need to enlarge on its importance and significance. "The history of chemistry cannot take the view that outstanding scientific discoveries, new generalizations, and the beginnings of new important trends in the evolution of chemistry are chance events," continued Figurovsky. "It is obvious that, in the external circumstances of Lomonosov's work and in the scientific activity itself of that great scientist, there existed deep roots, which at a definite moment gave out powerful shoots of the new scientific discipline of physical chemistry". The speaker made an analysis of the reasons for the remarkable discoveries of M. V. Lomonosov. The breaking up of feudal society, the growth and spreading of commercial capital, and the rise of capitalist industry in the West and of native manufacturing concerns based on serfdom in Russia (owned by the Demidovs, Stroganovs, and others) all had their effects on the grave upheavals that occurred in the productive efforts of society. Reorganization of the social-economic structure of society occurred, and in the middle of the eighteenth century a new epoch began in the evolution of science and technology — an epoch of great technological changes, inventions, and scientific discoveries. The whole scientific activity of Lomonosov reflected the upheavals that were occurring in the economy of the country. Lomonosov was an innovator in science and an enemy of traditional routine: his work was based on the rejection of old, traditional, misleading ways in science and on the search for new ways of progress. He boldly blazed new trails in all that he undertook — here lies the reason for his remarkable discoveries, here lies the greatness of his scientific creativity.

The development of Lomonosov's capacity for critical thought was influenced greatly by his broadly based education and by the training that he had received in mathematics, physics, and chemistry, which was no doubt facilitated by the process of emancipation from set traditions that was going on in science at that time.

The majority of workers in chemistry who were forerunners or contemporaries of Lomonosov were medical men by education and profession and were enslaved by traditional pharmacy, regarding chemistry as the art of preparing medicines, and not as a science. Lomonosov examined the contents of chemistry from the point of view of a scientific investigator and materialist who had rejected the traditions and prejudices of his time. The starting point and basis of his "Course of True Physical Chemistry" was his system of corpuscular philosophy, which he had worked out in its basic details and which formed the basis of his scientific work. Another starting point in the writing of the "Course of True Physical Chemistry" was to be found in the teaching activities of Lomonosov, who had an ardent desire to pass on the knowledge he had acquired to the youth of Russia.

Figurovsky showed in his paper that, whereas those not acquainted with the history of chemistry had asserted that Lomonosov gave us only the name "physical chemistry", he, in fact, created in the middle of the seventeenth century a complete scientific system on the basis of atomistics that was quite new at that time. By the aid of atomistics, Lomonosov developed ideas about chemical processes, explained many phenomena, and created a number of theories.

Prof. S. V. Gorbachev showed in his paper "M. V. Lomonosov's Investigations on Solutions" the way in which M. V. Lomonosov correctly estimated the significance of the theory of solutions in physical chemistry. Lomonosov was the first to distinguish dissolution processes from reactions such as the "dissolution" of zinc in sulfuric acid, and he formed the conviction that the heat change in the process could serve in practice as a criterion for the distinguishing of reactions and solution processes. Lomonosov's ideas on the nature of the heats

of solution and of chemical reaction were expounded by him theoretically in such a convincing fashion that they retained their significance and recognition for a century and a half. Berzelius in 1842 repeated Lomonosov's views almost in full. The speaker described the transition from Lomonosov's principle to the new, more profound principle of Mendeleev, which, while not rejecting the effect of the mutual attraction of particles with chemical combination and evolution of heat, supplemented these ideas by consideration of accompanying physical processes that have their own thermal effects. The theoretical views of M. V. Lomonosov turned out to be extremely fruitful: on its basis and on the paths of its further development were founded the theory of the passage of electricity through solutions, the concept of osmotic pressure, the theory of electrolytic dissociation, and the theory of strong electrolytes.

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Note: Because of its particular interest to researchers in the field of organo-phosphorus compounds, we have printed a number of extra copies of this issue, which will be available, at $20.00 each copy, so long as the supply lasts.
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